This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

Per 97

HARVARD UNIVERSITY

LIBRARY OF THE

Department of Mining
and Metallurgy

THE

SCHOOL OF MINES QUARTERLY,

A

JOURNAL OF APPLIED SCIENCE.

VOL. XXV.

NOVEMBER, 1903, TO JULY, 1904.

COLUMBIA UNIVERSITY,
NEW YORK CITY.

1904.

MAY 19 1908
Mining & Met. Laboratory

BOARD OF EDITORS.

A. J. MOSES, Prof. of Mineralogy.
J. F. KEMP, Prof. of Geology.
R. PEELE, Adj. Prof. of Mining.
R. E. MAYER, Adj. Prof. of Drawing.
E. WALLER, Analytical Chemist.
W. H. FREEDMAN, E.E.
T. H. HARRINGTON, Tutor in Drawing

Managing Editor R. E. MAYER.
Business Manager, T. H. HARRINGTON.

THE SCHOOL OF MINES QUARTERLY.

INDEX, VOL. XXV.

November, 1903, to July, 1904.

All Abstracts are Printed in Italics, and those relating to Chemical Analysis appear only under the heading Analytical Chemistry.

	PAGE.
Abstracts in Mineralogy, see Mineralogy, Abstracts.	
Aluminothermics. By Dr. Hans Goldschmidt	302
ALUMNI AND UNIVERSITY NEWS	105
Departments :	
Chemistry	105
Civil Engineering	111
Electrical Engineering	112
Geology	113
Mineralogy	109
Mechanical Engineering	113
Analytical Chemistry, abstracts. By Elwyn Waller.	
Alkalies in Presence of Borates	328
Alkalimetry.—Material for Standardizing	327
" , *etc.—Potassium Tetroxalate for Standardizing*	327
Alumina, Direct Determination	329
" *-Separation from Iron*	329
Ammonia Determination	328
Analysis of Iridosmine	333
Antimony in Commercial Lead	332
Arsenic and Antimony in Nickel Speiss	332
Bismuth Estimation	335
Boric Acid Determination	339
" " *in Presence of Stronger Acids*	339
Bromates, Estimation	337
Calcium, Conversion of Oxalate and Sulphate	329
Cerium Separation	336
Chlorates, Bromates and Iodates	336
Colorimetric for Bismuth	335
Commercial Lead.—Soft Lead	334
" *Nickel*	331

Decomposition of Galena and Chalcopyrite 334
Determination of Vanadium 336
Determining Chlorine in Presence of Carbon Dioxide 336
Estimating Persulphates 337
Examination of Asphalts 341
Ferro Silicon 338
Free Carbonic Acid in Water 339
" *Lime in Cements* 329
Gold, Iodometric Determination 333
Gravimetric Determination of Phosphoric Acid and Magnesia 338
Iodides, Action of Boric Acid 337
Lead Peroxide in Analytical Work 327
Nitric Acid in Nitrates, Volumetric 339
Organic Bases as Reagents for the Separation of Rare Metals 327
Portland Cement Distinguished from Slag Cement 340
Potable Waters — Iron and Phosphates 340
Potassium, Chlorimetric 328
" *Colorimetric* 328
" *Determination* 328
Reaction of Nitrites 339
Selenium and Tellurium Separation 335
" *Estimation* 336
Sensitive Indicator 327
Separating Tellurium from Antimony 335
Separation of Manganese and Iron 330
" " *Tin and Antimony* 333
Silver Cyanide 335
Sulphur in Coal and Coke 338
Sulphuric Acid Determination 337
Titanium, Qualitative 330
Zinc Determination 330
" *-Ferrocyanide Method* 330
ARENDT, M. & CROCKER, F. B. *Electrochemical Industries* 1
BENJAMIN, DR. MARCUS. *Address on Hamilton Young Castner* 214
Book Reviews:
Engineering and Mining Journal, N. Y. and London, 1903 116
Machine Design, Pt. 1. By W. L. Cathcart 117
Mineral Industry, Vol. 11 116
Proceedings of the Chemical and Metallurgical Society of South Africa, with Appendix. Vol. 2 341
Quantitative Analysis for Mining Engineers. By Edmund H. Miller 428
Radium and Other Radio-Active Substances. By Wm. J. Hammer 118
Bridge, Railroad, The Detailed Design of a. By Wm. H. Burr & Myron S. Falk 256, 368
BURR, WM. H. & FALK, MYRON S. *The Detailed Design of a Railroad Bridge* 256, 368
CAMPBELL, WILLIAM. *Notes on Metallography* 390
CARTER, A. E. *The Sanitation and Proposed Sewerage System of Havana, Cuba* 99
Caster, Hamiltion Young, Unveiling of a Bronze Tablet in Havemeyer Hall to the Memory of. Dec. 16, 1902 204

Cerrillos Hills, New Mexico, The Geology of. By D. W. Johnson. Pt. 3..... 69
CHANDLER, PROF. CHARLES FREDERICK. *Address on Hamilton Young Castner*..... 204
CROCKER, F. B. & ARENDT, M. *Electrochemical Industries*..... 1
Crucible Charge for Gold and Silver in Zinc Ores. By E. J. Hall & E. Popper. 355
Crystal Habit, A Method for the Exact Expression of. By A. F. Rogers..... 199
Detailed Design of a Railroad Bridge. By Wm. H. Burr & Myron S. Falk.. 256, 368
Dynamometer, A Simple. By W. J. Spiro..... 343
Electrochemical Industries. By F. B. Crocker & M. Arendt..... 1
Elementary Lecture on the Method of Least Squares. By Harold Jacoby..... 287
Engineering Cost Data, Gathering. By H. P. Gillette..... 358
FALK, MYRON S. & BURR, WM. H. *The Detailed Design of a Railroad Bridge*..... 256, 368
FINLAY, GEORGE IRVING. *Geology of the San Pedro District, San Luis Potosi, Mexico*..... 60
Formulæ for Calculating the Size of Wire Ropes. By Sheldon Smillie..... 194
Gathering Engineering Cost Data. By H. P. Gillette..... 358
Geology of the Cerrillos Hills, New Mexico. By D. W. Johnson. Pt. 3..... 69
Geology of the San Pedro District, San Luis Potosi, Mexico. By G. I. Finlay.. 60
GILLETTE, HALBERT P. *Gathering Engineering Cost Data*..... 358
GOLDSCHMIDT, DR. HANS. *Aluminothermics*..... 302
HALL, E. J. & POPPER, E. *A Crucible Charge for Gold and Silver in Zinc Ores*..... 355
Havana, Cuba, The Sanitation and Proposed Sewerage System of. By A. E. Carter..... 99
JACOBY, HAROLD. *An Elementary Lecture on the Method of Least Squares*.... 287
JOHNSON, DOUGLAS WILSON. *The Geology of the Cerrillos Hills, New Mexico*. Pt. 3..... 69
Least Squares, An Elementary Lecture on the Method of. By Harold Jacoby... 287
LUQUER, LEA MCI. & MOSES, A. J. *Notes on Recent Mineralogical Literature*..... 412
Metallography, Notes on. By Wm. Campbell..... 390
Method for the Exact Expression of Crystal Habit. By A. F. Rogers..... 199
MILLER, E. H. *Notes on Quantitative Analysis for Mining Engineers*... 21, 119, 221
Mineralogy, Abstracts. By A. J. Moses and L. McI. Luquer.
Crystallography and General Mineralogy..... 412
Individual Species.
Anthophyllite..... 421
Arsenic..... 421
Arsensulfurite..... 421
Artinite..... 422
Astrolite..... 422
Autunite..... 422
Boothite..... 422
Bornite..... 422
Botryogen..... 422
Carbides and Silicides..... 423
Cerussite and Phosgenite..... 423
Coloradoite..... 423
Coolgardite..... 423

Diamond 423
Euxenite 424
Fayalite 424
Gold 424
Kalgoorlite 424
Kœnenite 424
Krennerite 425
Molybdenite 425
Mohsite 425
Mooraboolite 425
Palacheite 426
Phosgenite 426
Proustite 426
Pyknochlorite 426
Rœsslerite 426
Sperrylite 426
Samarskite 427
Spodumene 427
Vesuvianite 427
Wapplerite 427
Zeophyllite 427
Mining Engineers, Notes on Quantitative Analysis for. By E. H. Miller.. 21, 119, 221
MOSES, ALFRED J. & LUQUER, LEA MCI. *Notes on Recent Mineralogical Literature* 412
Notes on Metallography. By William Campbell 390
Notes on Quantitative Analysis for Mining Engineers. By E. H. Miller.. 21, 119, 221
Notes on Recent Mineralogical Literature. By A. J. Moses & L. McI. Luquer 412
POPPER, E. & HALL, E. J. *A Crucible Charge for Gold and Silver in Zinc Ores* 355
Quantitative Analysis for Mining Engineers, Notes on. By E. H. Miller..21, 119, 221
Restant Source of Error in Optical Sugar Analysis. By F. G. Wiechmann..... 183
RICHARDS, DR. JOSEPH W. *Address on Hamilton Young Castner* 218
ROGERS, AUSTIN F. *A Method for the Exact Expression of Crystal Habit*..... 199
Sewerage System, Proposed, and Sanitation of Havana, Cuba. By A. E. Carter 99
Sanitation and Proposed Sewerage System of Havana, Cuba. By A. E. Carter.. 99
San Pedro District, San Luis Potosi, Mexico, Geology of the. By G. I. Finlay.. 60
Simple Dynamometer. By W. J. Spiro 343
Smillie, Sheldon. Formulæ for Calculating the Size of Wire Ropes 194
SPIRO, W. J. *A Simple Dynamometer* 343
Sugar Analysis, Optical, A Restant Source of Error in. By F. G. Wiechmann.. 183
Unveiling of a Bronze Tablet in Havemeyer Hall to the Memory of Hamilton Young Castner, Dec. 16, 1902 204
WIECHMANN, F. G. *A Restant Source of Error in Optical Sugar Analysis*..... 183
Wire Ropes, Formulæ for Calculating the Size of. By Sheldon Smillie..... 194
Zinc Ores, A Crucible Charge for Gold and Silver in. By E. J. Hall & E. Popper 355

VOL. XXV. No. 1. NOVEMBER, 1903.

THE

SCHOOL OF MINES QUARTERLY.

A

JOURNAL OF APPLIED SCIENCE.

BOARD OF EDITORS.

A. J. MOSES, Prof. of Mineralogy.
J. F. KEMP, Prof. of Geology.
R. PEELE, Adj. Prof. of Mining.
R. E. MAYER, Adj. Prof. of Drawing.
E. WALLER, Analytical Chemist.
W. H. FREEDMAN, E.E.,
T. H. HARRINGTON,
Tutor in Drawing.

Managing Editor, R. E. MAYER,
Business Manager, T. H. HARRINGTON.

CONTENTS:

Electrochemical Industries. By F. B. Crocker and M. Arendt 1
Notes on Quantitative Analysis for Mining Engineers. By Edmund H. Miller..... 21
Geology of the San Pedro District, San Luis Potosi, Mexico. By George Irving Finlay, Ph.D 60
The Geology of the Cerrillos Hills, New Mexico. By Douglas Wilson Johnson..... 69
The Sanitation and Proposed Sewerage System of Havana, Cuba. By A. E. Carter..... 99
Alumni and University News 105
Book Reviews..... 116

COLUMBIA UNIVERSITY

NEW YORK CITY.

Registered at the New York Post Office as Second Class Matter.

TWO DOLLARS PER YEAR. FIFTY CENTS PER NUMBER.

All Remittances should be made payable to Order of "The School of Mines Quarterly."

Portland Cement

THE LAWRENCE CEMENT CO.

ESTABLISHED 1832.

ERNEST R. ACKERMAN, President

This Company has manufactured and sold during 70 years upwards of **20,000,000** barrels of Cement; marketing the product in all the principal cities of the United States, Canada, West Indies, Philippines and South America.

The old Custom House on Wall Street, built in 1835–37, and the new Custom House on Bowling Green, now under construction, were built with cement sold by this Company.

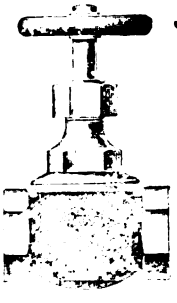
Used on the Old and on the New Stock Exchange in New York City, on the Brooklyn Bridge and New East River Bridge, and on the new Chamber of Commerce Building.

Detailed list of important Government Work. Reservoir Dams, Sidewalks, Fortifications, Bridges, Municipal Buildings and Railroad Work where "DRAGON" has been used, furnished on application.

DRAGON PORTLAND CEMENT Stands the Highest Requirements of Architects, Engineers and Builders.

SALES OFFICES:

NEW YORK, No. 1 Broadway. 15th and Market Sts., PHILA.



JENKINS BROS.' VALVES

The metal and workmanship are the best. All parts are interchangeable. Need no re-grinding as they are more effectively repaired by renewing the disc, which can be easily and quickly done without removing valve from the pipe, and costs but a trifle. Insist on having the genuine, which always bear our Trade-Mark.

Jenkins Bros., New York, Boston, Philadelphia, Chicago, London.

THE

SCHOOL OF MINES QUARTERLY.

VOL. XXV. NOVEMBER, 1903. No. 1.

ELECTROCHEMICAL INDUSTRIES.*

BY F. B. CROCKER AND M. ARENDT.

The word electrochemical is here used to include electrometallurgical as there is no generic term for the two subjects. Electrochemistry may be defined as that branch of science relating to the electrical production of chemical substances and chemical action or to the generation of electrical energy by chemical action. On the other hand electrometallurgy is the branch of science that relates to the electrical production and treatment of metals. The two subjects are based upon the same principles, the theory, laws and data of one being applicable to the other. Hence, it is proper and now customary to combine them under the head of electrochemistry.

Electrochemistry may be subdivided as follows:

A.— ELECTROLYTIC CHEMISTRY, which consists in separating or producing other action upon chemical substances by the decomposing effect of an electric current or vice versa. Since the electrolyte is usually in the liquid state, there are:

"Wet methods" with solution.

"Dry methods" with fused materials.

In the latter case the materials are maintained in a state of fusion by the heat due to the electrolytic current or by external heat.

Electrolytic chemistry is applied to the following purposes:

1. *Primary batteries* including various forms of voltaic cell in which electrical energy is generated by chemical action.

2. *Secondary or storage batteries* are similar to the foregoing, but

* Portion of lecture notes on electrochemistry, Electrical Engineering Department, Columbia University.

the chemical action must be reversible, so that after periods of working the cell may be charged or brought back to an active condition by sending through it a current opposite in direction to that which it generates.

3. *Electrotyping* is the art of reproducing the form of type and other objects by electrodepositing metal on the object itself or on a mould obtained from it.

4. *Electroplating* is the art of coating articles with an adherent layer of metal by electrodeposition, as in nickel plating.

5. *Electrolytic refining of metals and chemicals* by the elimination of impurities, as in the conversion of crude copper into pure metal.

6. *Electrolytic production of metals and chemicals*, as in the Hall process for extracting aluminum from alumina dissolved in fused cryolite, and in the Castner process for making caustic soda and chlorine from a solution of common salt.

7. *Electrolytic chemical effects*, such as bleaching, tanning, etc.

8. *Electrolytic chemical analysis*, as in copper determination.

B. — ELECTROTHERMAL CHEMISTRY includes those methods in which electric current raises the temperature of materials, usually to a high degree, in order to produce fusion, chemical action or other effects. Since electrolysis is not desired an alternating current is generally employed.

9. *Chemical action with electrical heating*, as in the production of calcium carbide from lime and carbon in an electric furnace.

10. *Electrical smelting* consists in reducing metallic compounds at a high temperature produced by an electric current, as in the reduction of iron ore in an electric furnace, or in the Cowles process for making aluminum bronze from a mixture of alumina, carbon and granulated copper.

11. *Electric fusion of chemicals*, usually those that are very refractory, such as silica and alumina. It has been proposed to make bricks by melting instead of baking the clay; electric heat has been used in furnaces for melting glass.

12. *Electrical heating and working of metals* consists in treating metals mechanically with the aid of heat generated by electric currents, as in electrical welding, forging, rolling, casting, tempering, etc.

Strictly speaking, the last two applications are not chemical, but some chemical actions usually occur and they are similar to the others in methods and results, so that it is customary to consider them under the head of electrochemistry.

C. Chemical Action Due to Electrical Discharges.

13. *Chemical effects of electrical arcs* to produce combinations of nitrogen and oxygen, for example.

14. *Chemical effects of electric sparks.*

15. *Chemical effects of silent electrical discharge*, as in the production of ozone.

Historical Notes. — The first electrochemical apparatus was the primary battery invented by Volta in 1799. The next year Nicholson and Carlisle discovered the chemical action of the electric current in decomposing water. In 1807 Sir Humphrey Davy gave his famous lecture "On Some Chemical Agencies of Electricity," he having, the same year, discovered the metals sodium and potassium by reducing their compounds electrolytically. In 1834 Faraday established definite laws and nomenclature for electrochemistry. From 1836 to 1839 Jacobi, Spencer, Jordan and Elkington applied these principles to practical use in the making of electrotypes. Planté began the development of the storage battery in 1859. Since that time, but mostly after 1886, the theory and applications of electrochemistry have made great progress, so that now it is one of the most important branches of science as well as of industry.

Primary and secondary batteries are prominent objects in electrochemistry, but it is customary to treat them under the general head of electricity or in special treatises.

Electroplating and electrotyping are electrochemical arts, but are usually considered as a separate branch and so treated.

The Electrolytic Refining of Copper.

The largest and most important of all electrochemical industries is the refining of copper, which is conducted at many places in this country and abroad. The process of refining copper electrolytically consists in the transfer of copper from the anode to the cathode, by the selective action of the electric current, and in leaving the impurities behind in the anode, electrolyte, and in the slime or sediment.

It is evident, theoretically, that the mere transference of copper should require no expenditure of energy, because metallic copper is both the raw material and the product; the energy needed to precipitate it from its solution being balanced by the energy set free upon its change to copper sulphate, but practically some

energy is needed on account of the resistance of the electrolyte, and differences in mechanical structure as well as in chemical purity of the anode and cathode.

The material at present subjected to profitable electrolytic refining is crude copper containing from 96 to 98 per cent. pure copper and varying amounts of other elements according to the character of the ore and method of dry refining adopted. The composition of the crude material varies greatly, typical samples being given in the following table:

	I. Per Cent.	II. Per Cent.	III.* Per Cent.
Copper	96.35	97.19	98.60
Arsenic	0.08	2.68	0.80
Antimony	0.10	0.01	0.10
Lead	1.19	.....	0.10
Tin	0.22	.....	.....
Bismuth	0.05	0.08	0.05
Iron	0.61	0.02	0.10
Nickel	.....	0.02	0.10
Sulphur	0.69	.....	0.10
Silver	.....	.....	0.05
Oxygen and loss	0.71	.....	
	100.00	100.00	100.00

Besides these, the crude copper frequently contains small quantities of gold (about one tenth to one fifth ounce per ton).

The crude material is cast in iron moulds into anode plates, which are about three feet long, two feet wide, and one inch thick, weighing approximately 250 pounds. The cathode plates are of electrolytically refined copper practically the same in length and width as the anodes but only one twentieth inch thick. The electrolyte or bath in which the plates are suspended is a solution of twelve to twenty per cent. copper sulphate, and four to ten per cent. sulphuric acid, the latter being added to decrease the resistance of the solution. This resistance is further reduced by keeping the electrolyte warm, about 40° C.

The containing tanks are of wood, usually lined with sheet lead or carefully coated with a pitch compound, and of such dimensions that a distance of about one inch exists between the faces of the plates.

In some cases the plates are arranged in series, and in others in parallel or multiple as illustrated. The former has the advantage of requiring electrical connections to be made at the first and last

* Chili Bar.

plates only, whereas the parallel system requires a connection at every plate, but in the series system the leakage of current due to the short-circulating action of the sediment and sides of the tank,

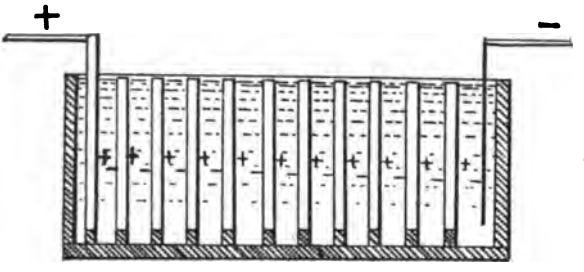


FIG. 1. Series Arrangement of Plates.

is from ten to twenty per cent., so that the parallel is more generally used.

The connections between the various plates and the circuit in the parallel systems, are made by copper rods, which are run at two different levels along the edges of the tanks, one bar for anodes and one for cathodes. In some instances these rods are of the inverted V shape, so that the edges will cut through any corrosion that may happen to form at the points of contact. The drop in pressure at these points is not more than .01 volt. The vats are

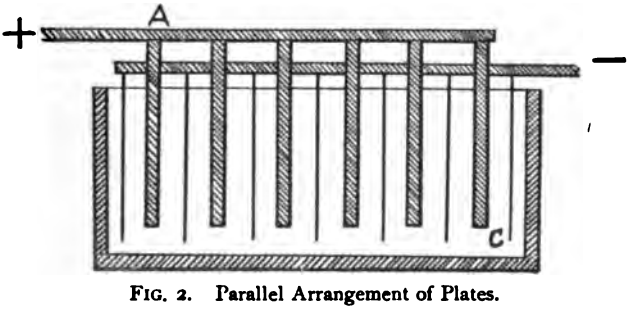


FIG. 2. Parallel Arrangement of Plates.

arranged so that each is accessible from all sides, and the circulation of the electrolyte is possible. This circulation may be obtained by blowing a stream of air through the electrolyte, but more frequently, by arranging the vats in steps and connecting them by pipes so that the electrolyte may pass from the top of one vat to the bottom of the next, as shown in the illustration. This maintains a uniform density of the electrolyte, which is necessary for the proper formation of the deposit.

The electrical pressure required is from .2 to .4 volt per tank, with a current density of ten to fifteen amperes per square foot of cathode plate surface. The individual vats are connected in series with each other, so that the total voltage required may be approx-

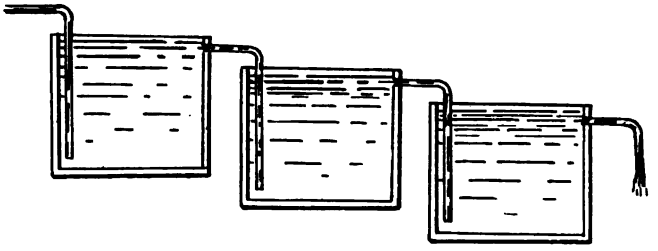


FIG. 3. Circulating System.

imately equal to that of the generator allowing the usual drop of about 10 per cent. Standard generators are built to give 125 volts so that a working pressure of about 110 volts is obtained which is a standard value for lighting and other purposes.

In practice from 400 to 500 ampere-hours are required per pound of copper deposited, the theoretical amount according to Faraday's law being only 386.2 ampere-hours. The loss varies from four to twenty per cent. according to the system employed.

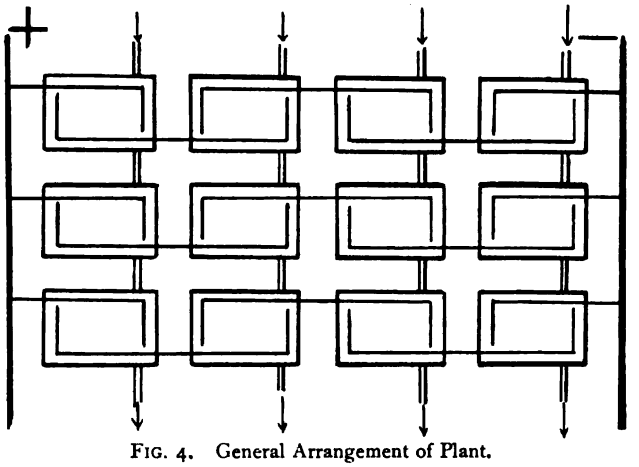


FIG. 4. General Arrangement of Plant.

The behavior during refining of the various impurities present in the anode plates is practically as follows:

Silver and gold remain undissolved in the anode sludge as metals, lead remains as a sulphate. Antimony, bismuth and tin are

partly dissolved out of the anode to form unstable sulphates which precipitate as basic sulphates or oxides upon standing; the larger part, however, of each remains in the anode sludge. Arsenic, nickel and iron dissolve and are not redeposited; thus they contaminate the electrolyte, but do not injure the purified copper under ordinary working conditions. Cuprous oxide and copper sulphide remain partly in the sludge and partly dissolve according to the acidity of the electrolyte, their only evil effect is to neutralize some of the free sulphuric acid.

The composition of the anode sludge (residue) will evidently vary according to the composition of the anode employed, and various amounts of gold, silver and lead are obtained therefrom.

The cost of refining copper by the electrolytic method is from one fourth to three fourths cent per pound. The following products of refining are marketed: commercial cathodes which are sometimes shipped to consumers, but more frequently cast into wire bars, ingots, cakes or slabs of standard dimensions and weight. They usually assay from 99.86 to 99.94 per cent. of pure copper, a sample analysis being as follows:

	Per Cent.
Copper*	99.938
Antimony	.002
Iron	.004
Oxygen and loss	.056
	100.00

The yield in commercial cathodes is from 97 to 99 per cent. of the anodes treated, excluding the anode scrap which varies from 7 to 15 per cent. of the original anode in parallel operated plants, but this scrap is not a loss, as it is collected and recast into anode plates. Besides electrolytic copper, most plants recover gold, silver and nickel from the slime as previously stated.

The electrolytic copper refineries in the world are now producing copper at the rate of 322,295 tons annually, valued at $96,688,500 with copper selling at $300 per ton, in addition the by-product in recovered gold and silver is valued at $20,000,000 per annum. There are now in active operation 33 electrolytic copper refineries, with a total generator capacity of 20,000 kilo-

* This sample was obtained by refining the crude copper given in column III. of the preceding table of crude copper anodes.

watts, 10 of these are located in the United States, and supply about 86 per cent. of the world's output; 6 plants are in England and Wales, producing about 9 per cent., while the remaining plants are on the continent of Europe.

Aluminum. — Practically the output of this metal for the entire world is now produced electrolytically. The only process used on a large scale is that invented independently in 1886 by Mr. Charles M. Hall in the United States, and by Paul L. V. Héroult in France. This process consists in electrolyzing alumina dissolved in a fused bath of cryolite. The alumina is obtained from the mineral bauxite which occurs abundantly in Georgia, Alabama and other regions. The natural material, being a hydrated alumina containing silica, iron oxide and titanic oxide, must be treated in order to drive off the water and eliminate the impurities. Formerly this was accomplished by a chemical process, but now it is effected more simply and cheaply by heating the material mixed with a little carbon as a reducing agent in an electric furnace. The impurities are thus reduced and collect as a metallic regulus in the bottom of the mass. This leaves the alumina nearly pure and it may be tapped off while fused or easily separated by breaking it up after cooling. In practice it requires two pounds of alumina for each pound of aluminum produced. The flux or bath in which the alumina is dissolved consists of cryolite, a natural double fluoride of aluminum and sodium ($Al_2F_6.6NaF$) found in Greenland. This is melted in a large carbon-lined, sheet iron tank, which constitutes the negative electrode, a group of suspended carbon rods forming the positive electrode. A direct current of about 65 H. P. at 5 to 6 volts is used. Only a portion of this voltage is required to decompose the alumina, the balance amounting to about two or three volts represents the heat produced which keeps the bath at the proper temperature and fluidity necessary for electrolysis — 850 to 900° C.* The passage of the current causes the aluminum to deposit on the bottom of the tank as a fused metal, being drawn off periodically. The oxygen set free combines with the carbon of the positive electrodes and passes off as carbonic oxide. The reaction is $Al_2O_3 + 3C = 2Al + 3CO$. About one pound of carbon is consumed for one pound of aluminum produced. When the alumina becomes exhausted from the bath, the voltage rises and lights a lamp

* This method of using the same current for heating and electrolyzing is covered by C. S. Bradley's U. S. Patent No. 468,148 of 1892.

shunted across the electrodes, thus giving notice that more material is needed. Each electrical horse-power produces about one pound of aluminum per day of 24 hours. According to Faraday's law the weight of aluminum deposited by 1,000 amperes is .743 lb. per hour. The actual yield of metal by the Hall process is about 85 per cent. of this theoretical amount.

The aluminum obtained averages 0.1 per cent. iron, 0.3 per cent. silicon, with traces of copper, titanium and carbon, but is guaranteed over 99 per cent. pure. The selling price of aluminum of this purity is about 31 cents per pound in large lots.

The metal when drawn from the tanks is cast into rough ingots which are afterwards remelted and converted into commercial shapes, such as sheets, rods, wires, etc.

The total power used by the various works employing the Hall process, is very large and amounts to more than 15,000 H. P. in the United States and Canada. The total power employed in European plants operating under the Héroult patents is nearly as great.

Electrolytic Production of Caustic Soda.

The production of caustic soda (NaOH) and chlorine (Cl) by the electrolysis of common salt (NaCl) is readily realized experimentally ($NaCl + H_2O = NaOH + Cl + H$), but its successful accomplishment on a commercial basis is difficult, because of the secondary reactions which take place, forming a mixed product of caustic, salt and hypochlorite of soda. These difficulties are avoided by separating the caustic soda solution that is formed, by a porous diaphragm, or by drawing it off as soon as formed; and in some cases the metallic sodium deposited is absorbed in mercury or molten lead. The two most prominent systems for the electrolytic production of caustic soda and chlorine from common salt, are the Castner-Kellner and the Acker processes, one operating at moderate temperatures (40° C.) and the other at high temperatures (850° C.).

The Castner process employed in this country at Niagara Falls is as follows: The electrolytic tank consists of a slate box, 4 feet long, 4 feet wide and 6 inches deep, the joints being made by means of a rubber cement. Two slate partitions reaching within one sixteenth inch of the bottom (under which are grooves) divide the cell into three compartments, each 15 inches by 4 feet sealed

from each other by a layer of mercury covering the bottom of the tank to a considerable depth. The two end compartments through which the brine is passed are provided with carbon anodes, shaped like a rail section, the broader flange being placed about a half inch above the mercury. These compartments are provided with tight covers and exhaust pipes of rubber and lead to lead the chlorine away. The central compartment has an iron cathode composed of twenty upright strips and is supplied with pure water, which is drawn off whenever its specific gravity increases to 1.27, due to the presence of the manufactured caustic, while the liberated hydrogen is led from this chamber by means of pipes and used as a fuel for the concentration of the caustic. The tank is pivoted at one end on a knife blade and rests at the other on an eccentric, which raises and lowers that end of the tank about a half an inch once a minute

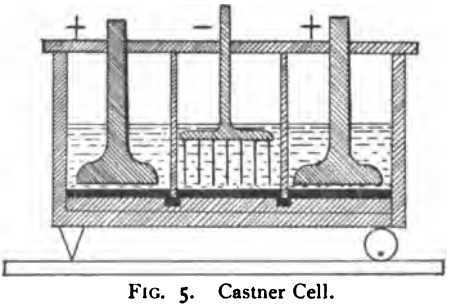


FIG. 5. Castner Cell.

and causes a circulation of the mercury between the outer and middle compartments. The current passes into the outer chambers, splits up the sodium chloride (common salt, NaCl) into sodium and chlorine (Na and Cl), the latter is liberated at the carbon anodes and passes through the exhaust pipe to the absorption chambers where it combines with slacked lime to form bleaching powder. The sodium combines with the mercury, forming an amalgam containing about 2 per cent. of sodium, which by the tilting of the tank passes to the central chamber, where it serves as the anode, and combines with the water to form caustic soda (NaOH) and hydrogen (H), the latter appearing at the iron cathode.

Each of these tanks uses 630 amperes at 4.3 volts; 10 per cent. of this current is shunted around the inner cell, because otherwise the amalgam would fail to deliver enough sodium, and the mercury would oxidize, thus producing mercury salts and con-

taminating the caustic. The theoretical voltage required is but 2.3, the remainder being utilized in overcoming the ohmic resistance of the electrolyte and in keeping it warm, the limit of temperature being 40° C., as above this point chlorate is formed. The output of this process per horse power per day is 12 pounds of caustic and 80 pounds of bleaching powder for each cell. The product contains from 97 to 99 per cent. caustic, ½ per cent. sodium carbonate, .3 to .8 per cent. of sodium chloride and traces of sodium sulphate and silicate.

The Acker process, also used at Niagara, for obtaining caustic soda and chlorine from salt is similar to the Castner-Kellner process just described, but differs in that it employs molten lead in place of mercury as a seal, fused salt instead of brine as the electrolyte and operates at a temperature of 850 degrees C. which is required to maintain the fused condition of the electrolyte. The containing vessel is a cast-iron tank five feet long, two feet wide and one foot deep, the sides above the molten lead being covered with magnesia so that the current must pass from the carbon anodes to the lead which acts as the cathode, the lower faces of the anode blocks being three fourths inch above the lead. At one end of the tank is a small compartment separated from the remainder of the vessel by a partition dipping into the lead to such a depth that nothing but this fused lead can pass from one compartment to the other. The chambers are loosely closed by fire clay slabs and the escaping chlorine drawn away through side flues by powerful exhausts. In the smaller compartment the lead is subjected to a stream of steam, which acting upon the lead sodium alloy forms caustic soda and liberates hydrogen. The steam jet is introduced below the surface, but points vertically upwards, and the resulting spray strikes a curved hood which deflects it into a third chamber in which the lead and caustic separate, the latter flowing out of the furnace over a cast-iron lip, the lead sinking and passing back to the main chamber, while the evolved hydrogen is conducted away. The fused caustic is collected in an iron pan where it solidifies and is removed every hour. The output is 25 pounds of solid caustic per hour. This process avoids the evaporation of the water required in the Castner-Kellner process. The current employed per vessel in the Acker process is 2,100 amperes at from 6 to 7 volts, of which energy 54 per cent. is used in chemical action and the remainder in maintaining the temperature.

Potassium chlorate is produced in considerable quantities both here and abroad. The Gibbs process used at Niagara Falls consists in the electrolysis of potassium chloride solutions, using a copper or iron cathode and a platinum anode. The cells are composed of a wooden frame, *A*, covered with some metal, *B*, such as lead, not attacked by the electrolyte. The latest form of cathode consists of a grid of vertical copper wires, *C*, kept in position by cross bars, *D*, of some insulating material, as shown in Fig. 6. The grid is placed in a vertical position against one side of the cell frame, and kept in place by the anode of the adjoining cell, from which it is insulated by the strips, *F*, and bars, *D*.

The opposite side of the cell from that occupied by the cathode is partially closed by the anode (see dotted lines of Fig. 6).

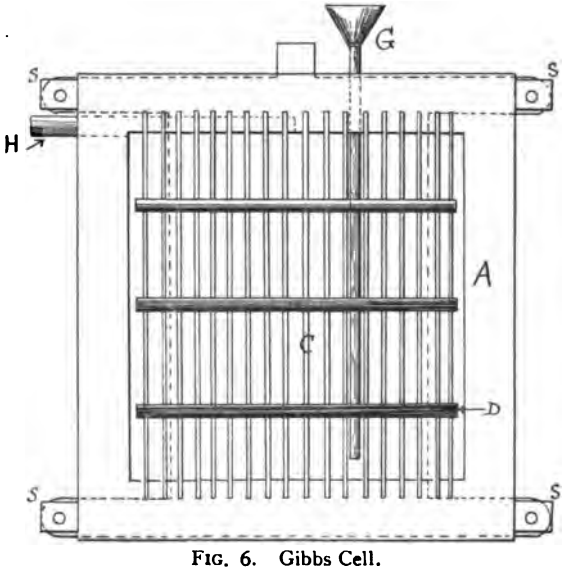


FIG. 6. Gibbs Cell.

This consists of a thick lead plate, *L*, covered with platinum foil on the outer side, *E*, Fig. 7. This anode is held in position by the cathode and framework of the following cell. *G* is the supply pipe, reaching to the bottom of the cell, by which the potassium chloride is continuously supplied to the cell, and *H* is the overflow pipe, used to convey the mixed solution of the chloride and chlorate, and liberated hydrogen gas are conveyed away from the cell. *S*, *S*, *S*, *S* are lugs projecting from the framework, by means of which any number of cells can be bolted together to form a series

of cells. Fig. 7 shows a group of three cells, the heavy plates (X and Y) being used to close the ends of the wooden framework, and form a fully closed series of cells with the only openings at the various supply and overflow points. The current connections are made at the points (m +) and (n —). When in nor-

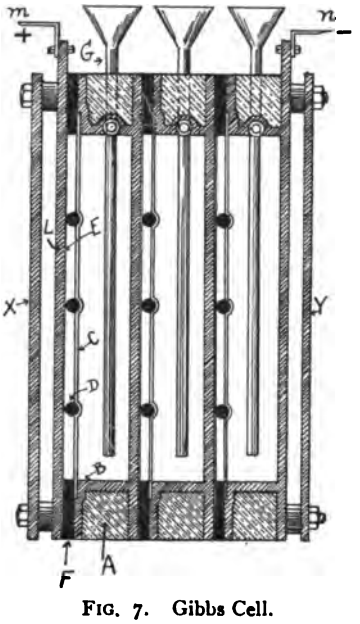


FIG. 7. Gibbs Cell.

mal working the cell is continuously fed by each of the supply pipes G, with a solution of potassium chloride, the rate of supply being so regulated as to maintain the temperature of the cell at 50 degrees C., and the amount of chlorate in the discharged solution slightly under 3 per cent.

Since the plates C and L of each cell are in metallic contact, due to the lead lining, the electrolysis occurs between the anode of one cell and the cathode of the following cell (see narrow space between cells), this space is small, not more than one eighth inch wide. The fact that the cathode is a grid allows the electrolyte to circulate around it and all the solution thus passes upwards and out of the cells at H.

The percentage of chlorate in the overflow solution is low, thus refrigeration is necessary to recover it, and Fig. 8 is a representation of an electrolytic chlorate plant using this form of apparatus.

S is the supply tank, *V*, the electrolytic cell; *R* the refrigerators, and *P*, the pump by means of which the exhausted electrolyte is returned to the supply tank, while the chlorate precipitates out as crystals. The reason for using the refrigerator is that in solutions containing only 3 per cent. of chlorate, the latter will not crystallize out upon natural cooling, as it would if present in large quantities. This low percentage of chlorate present is necessary to obtain quick recovery, as otherwise the presence of the hydrogen

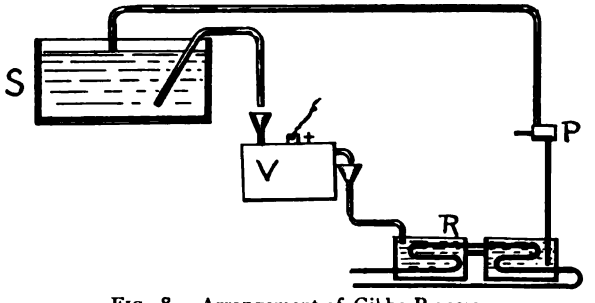


FIG. 8. Arrangement of Gibbs Process.

will cause secondary reactions, and cut down the efficiency of the conversion. The pressure employed is about four volts per cell, of which 1.4 is required to convert the chloride into chlorate

$$6KCl + 6H_2O + \text{Elect.} = 6KOH + \overbrace{3H_2} + \overbrace{3Cl_2}$$

$$6KOH + \overbrace{3H_2} + \overbrace{3Cl_2} = 2KClO_3 + 4KCl + \overbrace{3H_2}$$

and the remainder produces the heat that maintains the electrolyte at 50 degrees C. which is necessary for the proper reaction. The current density is high, about 500 amperes per square foot of anode surface. At Niagara the plant consists of fifty such cells, connected up into two sets of 25 cells in series. A direct current of 10,000 amperes is supplied at 175 volts, which allowing for line drop and losses at cell contacts gives the proper pressure.

Electrolytic chemical effects such as bleaching have been produced through the action of chlorine or other matter set free by an electric current. It is possible in this way to cause substances to act while in the nascent state and therefore more powerful. Disinfecting and deodorizing of sewage has also been accomplished in a similar manner, as in the Woolf process by the electrolysis of a salt solution mixed with the sewage. The passage of the current

liberates ($\widetilde{Cl_2}$) chlorine and sodium hypochlorite (NaClO), which act upon the refuse matter.

Electrolytic chemical analysis is a special subject, the discussion of which is usually confined to books and journals relating particularly to chemical analysis; it is not ordinarily considered in connection with the general subject of electrochemistry, and it would not be regarded as an electrochemical industry.

Calcium Carbide. — This compound is produced by an electrothermal process invented by Willson in 1891, the total output throughout the world being about 300,000 tons in 1902. Its value lies in the fact that 1 pound of this substance mixed with water produces theoretically 5.5 and actually about 5 cubic feet of acetylene, equivalent in illuminating power to about 70 cubic feet of ordinary gas. The reaction producing acetylene is $CaC_2 + H_2O = CaO + C_2H_2$. Various forms of electric furnace have been employed in the production of calcium carbide. One type invented

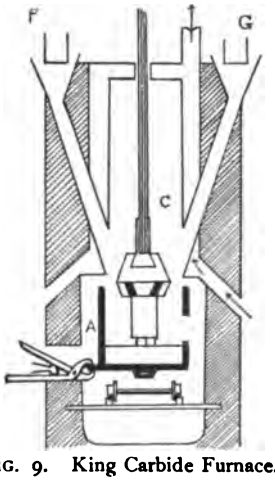


FIG. 9. King Carbide Furnace.

by King and represented in the illustration consists of an iron car, *A*, which holds the materials and carbide, at the same time acting as one electrode. It can be run into place or removed as desired, and being provided with trunnions its contents may be tipped out. The other electrode consists of a bundle of carbon plates carried by a heavy rod, *C*, composed of a copper strip strengthened by iron side bars. The material which is fed through the channels *G*, *F* consists of a mixture of 1 ton of burnt lime and three fourths ton

of ground coke to produce 1 ton of carbide, the reaction being $CaO + 3C = CaC_2 + CO$. An arc is first formed between the electrode *C* and the floor of the truck. The resulting high temperature converts the mixture into carbide, the electrode being gradually raised and more material added until the car is nearly filled with the product, when it is run out and replaced by another. At Niagara Falls a rotary form of furnace invented by C. S. Bradley is used, being operated continuously and producing about two tons in 24 hours when supplied with 3,500 amperes at 110 volts, or about 500 horse-power. Since no electrolytic action is required, an alternating current is employed.

Barium Compouuds. — The principal source of barium is barite or heavy spar, the natural sulphate. Processes for converting this material into barium hydrate, nitrate, chloride and other soluble salts have been invented by C. S. Bradley and C. B. Jacobs. They consist in melting in an electric furnace a mixture of barium sulphate with a small quantity of carbon. If five parts of sulphate to one part of carbon be present, all the sulphate would be reduced to sulphide, but with one fourth as much carbon a corresponding amount of sulphide is produced which reacts upon the rest of the sulphate and the oxide is obtained, the two reactions being as follows:

$$BaSO_4 + 4C = BaS + 4CO$$
$$3BaSO_4 + BaS = 4BaO + 4SO_2$$

The carbonic oxide (CO) and sulphurous acid (SO_2) pass off as gases, the latter being used to make sulphuric acid. The fused barium oxide (BaO) is tapped off, cooled, broken up and then digested with hot water. On cooling, barium hydrate [$Ba(OH_2)$, $8H_2O$] crystallizes out. This is used in extraction of sugar, treating hides, making white paints, "softening" water, and producing other barium compounds.

Cyanides of Potassium and Sodium are produced electrochemically by the process of C. S. Bradley, C. B. Jacobs and others. A mixture of barium oxide or carbonate with carbon is heated in an electric furnace to produce barium carbide (BaC_2). While the mass is still hot, nitrogen * is passed through it and barium cyanide forms, the complete reaction being:

$$BaO + 3C + N_2 = BaC_2N_2 + CO.$$

*Air cannot be used, as the oxygen present would oxidize the barium and the carbon.

The barium cyanide thus produced is treated with sodium carbonate, the result being a mixture of sodium cyanide and barium carbonate. The former is separated by dissolving it in water, the insoluble barium carbonate being used over again. Potassium cyanide is made in a similar manner and either salt is suitable for gold extraction and other purposes for which cyanides are employed.

Carborundum is a commercial name for carbon silicide (CSi) which is produced in large quantities according to the inventions of A. G. Acheson and his assistants. It is used as an abrasive, being hard enough to scratch ruby. It is formed by intensely heating in an electric furnace a mixture of three and one half tons of ground coke, six tons of sand and about one and one half tons of sawdust and salt, the yield being three or four tons of crystalline carborundum and about as much more of the amorphous material. The furnaces used at Niagara Falls consist of fire brick

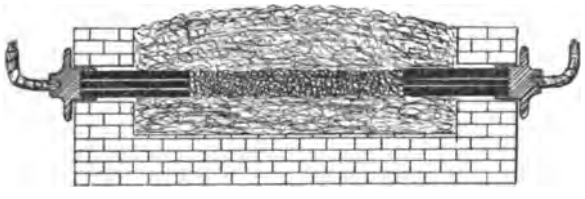


FIG. 10. Carborundum Furnace.

hearths sixteen feet long and five feet wide, with solid brick walls at each end about two feet thick and six or eight feet high as illustrated. In the middle of each of these walls there are iron frames through which the current is led to a core composed of carbon, weighing about 1,000 pounds and extending the entire length of the furnace. This core is raised to a very high temperature by passing through it for 36 hours an alternating current of about 1,000 electrical horse power at 190 decreasing to 125 volts. The heat from the core permeates the mass and converts it into carbon silicide which is broken up after the furnace has cooled and used to make hones, wheels for grinding, etc.

Artificial Graphite.—As an outgrowth of the carborundum process, Mr. Acheson has developed on a large scale the manufacture of artificial graphite. The material ordinarily used is anthracite coal ground to about the size of rice which is raised to an exceedingly high temperature in a long electric furnace in the form of a trough about 2 feet square and 30 feet in length. An alternating

current of about 1,000 horse-power at 220 decreasing to 80 volts is passed for 20 hours longitudinally through the mass which becomes converted into graphitic carbon. Another line of manufacture consists in graphitizing moulded articles of carbon such as blocks and rods for electrodes, which are piled in a furnace similar to that described for converting coal into graphite. By using different materials and conditions the two methods produce different kinds of graphite suitable for lubrication, crucibles, pencils, stove polish, electrodes, etc.

Alundum, the trade name for artificial corundum, is an abrasive made by a process due to C. B. Jacobs and others. Bauxite, a natural hydrated alumina, the same material as used in the Hall process, is calcined to drive off the water and then fed into an electric furnace, the construction of which is as shown in the illus-

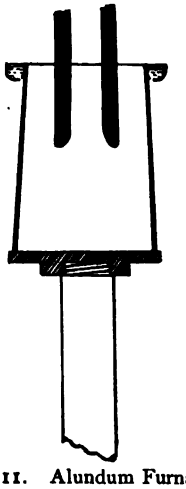


FIG. 11. Alundum Furnace.

tration, and it consists of a conical sheet-iron shell mounted on a hydraulically operated plunger, that raises and lowers it, to keep the current of 80 volts constant at 2,000 amperes. The electrodes consist of two carbon rods that project into the shell, which is cooled by water, from the U-shaped trough, trickling down its outer surface.

The time consumed for fusion is about 12 hours. The mass is allowed to cool and is then removed from the furnace, by holding the sheet-iron shell in position and lowering the plunger; in this manner the product is brought to the ground where it is broken up

and sorted. It consists of four parts; namely, a red and blue mass in the interior, crystals that form in the blow holes, a porous outer portion and a by-product consisting of a metallic regulus of ferro-silicon which is used for the treatment of iron in the Bessemer and open hearth furnaces. The porous outer part is used as a recharge, and the mass as well as the crystals, which are of the nature of rubies and sapphires, in fact chemically identical with these gems, are ground up and used to make grinding wheels, and general abrasives.

Electric Smelting.—One of the earliest commercial processes in electro-chemistry was that devised by E. H. and A. H. Cowles in 1884. A mixture of about 2 parts of alumina, 1 or 2 parts of granulated copper and 1 or 2 parts of carbon was introduced in a brick-work chamber. Bundles of carbon rods inserted at the ends formed the electrodes between which a current of 3,000 amperes at 50 volts was maintained. At a very high temperature the alumina was reduced ($Al_2O_3 + 3C = Al_2 + 3CO$) and the resulting aluminum combined with the copper to form aluminum bronze.

Iron and steel can be produced by reducing iron ore with carbon in an electric furnace. For example, a mixture of magnetite and carbon can be heated by passing a current through it as in the Cowles aluminum bronze process; through a carbon core in contact with the material as in the carborundum process; or by the action of an arc as in the carbide process. The reaction is simply $Fe_3O_4 + 4C = 3Fe + 4CO$. Pure (*i. e.*, wrought) iron, cast iron or steel may be produced, depending upon the proportion of carbon. The chief advantages are the directness of the process and the fact that the impurities in the fuel (sulphur, silicon, etc.) are not introduced. On the other hand, it is a question whether the electric furnace can compete in economy with the blast furnace and Bessemer converter.

Compounds of nitrogen and oxygen are produced by the electrical process of C. S. Bradley and D. R. Lovejoy. The apparatus consists of a cylindrical chamber through which a number of iron wire electrodes *EE* are introduced as illustrated. The ends of the radial arms *AA* carried by a revolving spindle *S* pass very close to the electrodes. A pressure of 6,000 to 8,000 volts maintained by the generator *C* between the arms and the electrodes produces arcs 4 to 6 inches long that are drawn momentarily. The current is unidirectional but being pulsating an inductance coil *C* in series

with each electrode cuts the current down to about .005 ampere per arc. There are 180 stationary electrodes in each chamber and as the arms revolve 500 or more times per minute at least 18,000 arcs are formed in each chamber in that time. Ordinary air after being dried is passed through the chamber where the arcs cause a certain percentage of the nitrogen and oxygen to combine. This compound absorbed in caustic soda forms sodium nitrite or nitrate;

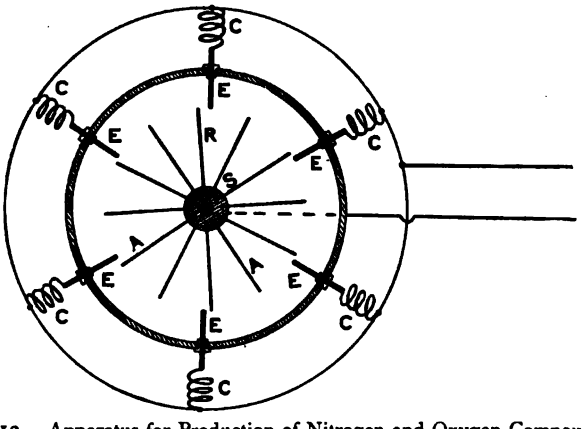


FIG. 12. Apparatus for Production of Nitrogen and Oxygen Compounds.

with potassium hydrate it forms potassium nitrite or nitrate, and by absorption in water nitric acid may be produced.

Ozone is produced in chambers through which a silent electric discharge is caused to pass from a static electric machine, induction coil or very high voltage transformer. If air circulates through the chamber a certain portion of its oxygen is converted into ozone.

Organic compounds, such as dye stuffs, vanillin, iodoform, chloroform are also produced electrically.

NOTES ON QUANTITATIVE ANALYSIS FOR MINING ENGINEERS.

By EDMUND H. MILLER.

Introduction.

These notes are intended primarily for the use of the students in the School of Mines at Columbia, so that some apology may be necessary for offering an article, which contains very little original material to the readers of the School of Mines Quarterly. These notes represent the methods as they are taught at present; and, while they can be found described elsewhere, it is often an advantage to the mining engineer as well as the student to have them collected and described as applied to technical analyses. Further, so many men now enter the mining course with advanced standing from other universities and schools, that it would seem desirable to show in this way what we require from our mining students in quantitative analysis.

The entire course will be covered, beginning with an introduction on some of the analytical applications of the theories of ionization, mass action and solubility product which are so important in understanding the reasons underlying many quantitative methods; then taking up the analysis of a few pure salts for practice in manipulation and next the analysis of the following natural and technical products: coal, iron ore, pig iron, spiegel and manganese ores, zinc ores, limestone, copper ores and mattes, ores of lead, arsenic, antimony, slags and flue gas.

In describing some well-known method it is not always possible to give to each chemist exactly the credit he deserves in its development, so that acknowledgment is made here to all the standard books on the subject, and special references are made only to the more recent journal articles. References will be given at the end of each chapter to both books and articles containing further information on the subjects.

CHAPTER I.

Ionization.

Chemistry to-day must consider, besides atoms and molecules, ions. Ion was the name given by Faraday to the moving particles in a solution which carried the electric current. Many years later, in 1887, Arrhenius, in attempting to explain the abnormally high osmotic pressures given by many aqueous solutions, discovered that only those solutions which conducted the current gave these high osmotic pressures, and so decided that there were present in such solutions particles other than molecules, which he designated by Faraday's name of ions.

Although there is now abundant evidence of the existence of ions, a few words on osmotic pressure may not be out of place, as it affords one of the most convincing proofs of ionization. It has been shown by experiment that the laws of gases in regard to pressure and temperature apply equally to substances in solution. Here the volume is the volume of the solution, and the pressure is not exerted, as in the case of gases, on the walls of the containing vessel; but requires for its detection a semi-permeable membrane of such a nature that the solvent can pass through, but the dissolved substance cannot. Such diaphragms were made by Pfeffer in 1877, and with them he showed that the osmotic pressure of such substances as sugar obeyed the gas laws; that doubling the number of molecules of sugar, dissolved in a given volume of water, doubled the osmotic pressure, and also that increasing the temperature increased the pressure in the same ratio as for gaseous molecules.

This important agreement having been shown for a number of substances, usually organic, it was found that there were many salts and other inorganic compounds, such as acids and bases, which did not obey the law, but which gave osmotic pressures greater than those calculated from the number of molecules present, so that, as the pressure depended on the number of particles, there must be more particles than molecules present. This gave rise to the theory of ionization or electrolytic dissociation which is: that many compounds, such as salts, when they are dissolved in water are disso-

ciated into ions, and that these smaller particles conduct the electric current and are the active elements in most chemical reactions. When a simple salt dissolves in water, such as sodium chloride, two ions are formed, $\dot{N}a$ and $\bar{C}l$; in this case the ions coincide in chemical formula with the atoms, but they differ chemically. If we place the metal sodium, with which we are familiar, in water, an immediate reaction results with the evolution of hydrogen and the formation of caustic soda; and also the familiar chlorine is a gas of disagreeable odor and active properties, which differs entirely from the chlorine ion. The difference between these elements in the ordinary and in the ionic condition is one of electric charge.

The ions do not always coincide with the atoms, however; when cupric sulphate is dissolved in water we have $\dot{\dot{C}}u$ and $\bar{\bar{S}}O_4$ ions, the solution being blue on account of the presence of the $\dot{\dot{C}}u$ ions; if a current of electricity is passed through such a solution the copper ions travel to the cathode; and as the positive charges of electricity they carry are neutralized by the negative current, the blue copper ions are converted to the red metallic copper which deposits on the cathode.

The electric charge carried by the equivalent weight in grams of any element or radicle is 96,540 coulombs, so to liberate one gram of hydrogen by the electrolysis of water we must supply 96,540 coulombs of electricity. As in cupric sulphate, copper is a diatomic element, the hydrogen equivalent is one half the atomic weight, so that 96,540 coulombs will deposit 31.8 grams; or we may say that the cupric ion carries a double charge of electricity. This is designated $\dot{\dot{C}}u$, to show two positive charges. The importance of this quantity of electric charge, not only from the theoretical, but also from the practical standpoint, is seen when we consider solutions of an element in two degrees of oxidation or where the ion has difference degrees of valence or of electric charge. Take, for example, solutions of cuprous and of cupric salts, with the cuprous there is but a single charge of electricity, with the cupric a double; so 96,540 coulombs will deposit from a cuprous solution 63.6 grams of copper and from a cupric 31.8: or if we consider the amperage, the same current will in the same time deposit twice the copper from a cuprous that it will from a cupric solution.

This shows the intimate connection which exists between the valence of an ion and its electric charge. It is accompanied often by marked physical differences.

Compare solutions of potassium manganate * and potassium permanganate, one green the other purple, but both composed of the same ions, K and MnO_4. The only difference is that with the manganate we have $\overset{+}{K}$, $\overset{+}{K}$ and $\bar{M}n\bar{O}_4$, while with the permanganate $\overset{+}{K}$ and $\bar{M}n\bar{O}_4$, the anion or negative ion has a double charge in the manganate. Similarly there is a difference between the colors of ferrous chloride and of ferric chloride depending on whether the Fe ion has two or three positive charges.

The following list † gives the most important cations and anions:

CATIONS.

Monovalent. — H in acids, K, Na, Li, Cs, Rb, Tl, Ag, NH_4, Cu (cuprous), Hg (mercurous).

Divalent. — Ca, Sr, Ba, Mg, Fe (ferrous), Cu (cupric), Pb, Hg (mercuric), Co, Ni, Zn, Cd.

Trivalent. — Al, Bi, Sb, Fe (ferric).

Tetravalent. — Sn, Zr.

ANIONS.

Monovalent. — OH in bases, F, Cl, Br, I, NO_3, ClO_3, ClO_4, BrO_4, MnO_4 (permanganates) and the anions of all other monobasic acids, *i. e.*, the acid molecule minus one hydrogen which goes to the kathode.

Divalent. — S, Se, Te, SO_4, SeO_4, MnO_4 (manganates) and the anions of dibasic acids.

Tri- to Hexavalent. — The anions of tri- to hexavalent acids. Elementary anions with a valence of more than two are not known.

The degree of ionization is measured most readily by finding the electrical conductivity of the solution, for this is dependent on the number of ions present and the rate at which they move; and is more convenient than obtaining the results from the osmotic pressure, on account of the difficulty in making diaphragms which shall resist these enormous pressures and at the same time not let through any of the dissolved substance. In this way it is shown that most organic compounds are practically undissociated into ions.

It is true that organic acids and bases are dissociated in aqueous solution, but the great majority of the important organic compounds, such as alcohols, ethers, carbohydrates, hydrocarbons, etc., are practically without appreciable ionization.

* Add a little alkali to prevent rapid decomposition.

† Taken from Ostwald's Scientific Foundations of Analytical Chemistry.

The extent of the ionization of some of the typical inorganic compounds is as follows: In a tenth normal solution most simple salts such as potassium sulphate, sodium nitrate, potassium chloride, ammonium chloride and so on, are almost completely dissociated. There are but few exceptions to this statement; one is the salts of cadmium and another those of mercury, the most important being mercuric chloride, and the fact that the nitrate gives many reactions which are not obtained from the chloride, may be explained by the inertness of the chloride, due to lack of dissociation into ions. With acids the dissociation is into hydrogen ions and negative ions consisting of the negative element or radicle as $\dot{H}, \bar{Cl}$; $\dot{H}, \bar{N}O_3$; $\dot{H}, C_2H_3O_2$; $\dot{H}, \dot{H}, \bar{S}\bar{O}_4$; $\dot{H}, \dot{H}, \bar{C}_2\bar{O}_4$, etc. The concentration of the hydrogen ions measures the strength of the acid. In a tenth normal solution the percentage of ionization is as follows: Hydrochloric acid, 99.5 per cent.; nitric acid, 100 per cent.; sulphuric acid, 69 per cent.; acetic acid, 1.4 per cent.; carbonic acid, 0.174 per cent.; sulphydric acid (H_2S), 0.075 per cent.; boric acid, 0.013 per cent. These values give definite expression to the ideas concerning the relative strength of acids though they contradict some of the old views: for instance, it has been often stated that sulphuric acid is the strongest, because it will displace other acids from their salts, but it is less ionized than hydrochloric acid, and the fact that when evaporated with sulphuric acid, chlorides are changed to sulphates, is explained by the easy volatibility of hydrochloric acid and is not a proof that sulphuric is the stronger acid.

Similarly the strength of a base depends on the concentration of the OH ions. At a dilution of tenth normal, potassium hydroxide is 100 per cent. dissociated, sodium hydroxide, 95.3 per cent. and ammonium hydroxide only 1.6 per cent. So that nitric and hydrochloric acids bear almost the same relation to acetic acid as the fixed caustic alkalies do to ammonia.

Ionization increases with dilution to a very marked degree so that at an infinite dilution all ionizable substances are completely dissociated. The effect of dilution is shown by the following values for monochloracetic acid: $N/2$, 5.4 per cent. dissociated; $N/8$, 10 57 per cent.; $N/32$, 20 per cent.

Temperature has but little effect on the degree of ionization, but a very considerable influence on the rapidity with which the ions travel; so that rise in temperature increases the conductivity of the solution as it increases the rate of migration of the ions, and there-

fore must be considered in calculating the ionization from the conductivity.

So far water alone has been considered as the solvent, as it has the greatest dissociating power; in other solutions the degree of ionization is much less; but water itself, although usually considered a non-conductor, is dissociated very slightly, and is found to contain one gram of hydrogen ions to twelve million liters. As will be explained later even this infinitesimal ionization makes water a reagent of importance in a number of quantitative reactions.

The reaction in neutralizing sodium hydroxide by hydrochloric acid is usually written: $NaOH + HCl = NaCl + H_2O$.

This represents the weights which take part in the reaction and if we evaporate off the water, the calculated quantity of sodium chloride will be obtained. But while in solution these substances are not all present as molecules, and if we perform the neutralization with solutions more dilute than tenth normal, so that the ionization of the acid, alkali and salt is practically complete, we shall have:

$$\dot{Na}|\bar{O}H + \dot{H}|\bar{Cl} = \dot{Na}|\bar{Cl} + H_2O$$

or on both sides of the equation we have Na and Cl ions, but instead of H ions and OH ions we have undissociated water. So that the essential part of this and every other reaction of neutralization is the formation of water. This is strikingly confirmed by the fact that the heat of neutralization of equivalent quantities of caustic alkali by different strong acids is the same, 13,700 calories for the equivalent weights in grams.

The following may emphasize the importance of considering what is present in a solution instead of what was dissolved to produce it: Suppose the formula weight in milligrams of potassium chloride and the formula weight in milligrams of sodium nitrate are dissolved together in a large volume of water so that the dissociation is complete; and that in another vessel in an equal large volume of water, the formula weights in milligrams of potassium nitrate and of sodium chloride are dissolved. The two solutions are identical for there are present in each the same number of the same four ions $\dot{Na}$, $\dot{K}$, $\bar{Cl}$ and $\bar{NO}_3$.

The characteristic colors of solutions are due either to the color of the ion or the color of the molecule. When solutions of nickel or copper are evaporated to fumes with sulphuric acid, they lose

their characteristic colors, for when the water has been removed there is no longer ionization—or color. Cobalt chloride dissolved in alcohol is blue, the color of the molecule; when water is added it becomes pink, showing the color of the ion. In the same way cupric chloride changes from brown to blue. The change in the colors of indicators is due to the passing from an ionized salt of the indicator to an undissociated molecule.

While it is not claimed that there is no reaction without ionization it is certain that in the case of aqueous solutions of inorganic compounds we are dealing with ionic reactions. In qualititative analysis most of the tests are tests for ions, as silver nitrate for the chlorine ion; but if sodium chlorate is dissolved in water and silver nitrate is added, no precipitate of silver chloride is produced; for though there is chlorine present there are no chlorine ions, as the dissociation is into Na and ClO_3. Also with a solution of sodium chlorplatinate there is no production of silver chloride but a yellow precipitate of silver chlorplatinate is formed, a test for the $PtCl_6$ ion.

When ammonia is added to a solution of ferric chloride or any other solution containing ferric ions, ferric hydroxide is formed; but no such reaction takes place when it is added to a solution of potassium ferricyanide, although it contains iron in the ferric condition, for the ionization is into K ions and $Fe(CN)_6$ ions. If a test for the $Fe(CN)_6$ ion is applied in each case, for example ferrous ions, nothing results with the ferric solution; while with the ferricyanide a characteristic precipitate is formed, Turnbull's blue.

As inorganic qualitative analysis is made up largely of such tests and separations, there is no lack of further illustrations of the application of the theory of ionization to this important branch of analytical chemistry.

CHAPTER II.

Mass Action.

In order to understand the most important effects of ionization on quantitative analysis, the law of mass action must be considered in an elementary way. This will be done by taking it up first in connection with molecular and then with ionic dissociation.

Dissociation was the name given originally by Deville to the separation of a molecule into smaller molecules by heat. For instance, when hydriodic acid gas is heated above 180°C. it begins to separate into hydrogen and iodine. This decomposition increases as the temperature is raised still further and decreases on lowering the temperature again, so that for hydriodic acid the amount of dissociation is always the same at a given temperature and pressure. This is often expressed as follows: $2HI \rightleftharpoons H_2 + I_2$ which shows that the reaction may go from right to left or from left to right depending on conditions. Ammonium chloride dissociates readily into ammonia and hydrochloric acid gases, so that when this process is complete, there will be present double the number of molecules and, according to Avogadro's law, double the pressure if the volume is unchanged. This is a disturbing feature in those methods of molecular weight determination which rely on vapor density determinations, for the molecular weight decreases with increasing dissociation as the temperature rises. With sulphur the molecular weight at low temperatures shows eight atoms in the molecule, while at 860°C. there are only S_2 molecules present. Ferric chloride gives values agreeing with the formula Fe_2Cl_6 at 320–440° but dissociates at higher temperatures. Nitric oxide is a mixture of NO_2 and N_2O_4, at ordinary temperatures, but if the the temperature is raised the density diminishes until at 150° it remains constant at 22.9 compared to H_2 as unity, which agrees closely with the calculated weight for NO_2.

In all such cases there is for each condition of temperature and pressure a definite state of equilibrium at which the proportion of the two gases is constant. If "reaction velocity" is considered as the rate at which this condition is approached, then the state of equilibrium will be that in which the reaction velocities are equal. In the

reaction $N_2O_4 \rightleftharpoons 2NO_2$. When the state of equilibrium is reached, just as much N_2O_4 is formed in each second by the combination of NO_2 as is dissociated into NO_2. While there is reaction going on, as the two effects are equal in amount and opposite in direction, the effect is nothing and a condition of equilibrium exists. The principle that the reaction velocity at any moment is proportional to the masses of the substances then present, is called the law of mass action.

Guldberg and Waage found that the rate of chemical action (reaction velocity) was proportional to the active mass of each of the reacting substances; that is, to the number of gram molecules or formula weights per liter, whether as a gas or in solution. The following instances illustrate how important the influence of mass is in some familiar reversible reactions: $CaCO_3 \rightleftharpoons CaO + CO_2$. At high temperature we have the condition of equilibrium disturbed, dissociation increases and if the active mass of carbon dioxide is decreased by removing the gas the tendency for the reverse reaction is checked and the reaction soon proceeds completely from left to right. On the other hand, when carbon dioxide is passed over cold lime the reverse reaction takes place.

When steam is passed over red-hot iron an oxide of iron is formed and hydrogen; while if the oxide is heated in a current of hydrogen aqueous vapor and metallic iron are produced. The action is reversible, depending on the active mass of the substances present; in the first case there can be no concentration of the hydrogen as it is constantly displaced by fresh quantities of steam; while in the second case the concentration of the steam is prevented by the current of hydrogen.

In accordance with this law, if to a dissociated substance one or more of the products of dissociation is added, the degree of dissociation is diminished, because the active mass is increased and the tendency to the reverse reaction strengthened. When phosphorus pentachloride is vaporized, it is very largely dissociated into phosphorus trichloride and chlorine. but if vaporized in an atmosphere of chlorine, this is prevented by the mass action of the chlorine and the molecular weight is found to correspond very nearly to that calculated for phosphorus pentachloride, instead of to about half that value.

These principles have a most important bearing on analytical chemistry: for instance, lead can be precipitated as sulphide, from

a solution very slightly acid with hydrochloric acid; while on the other hand lead sulphide, whether natural or artificial, can be dissolved readily in strong hydrochloric acid. This is evidently a reversible reaction.

$$PbS + 2HCl \rightleftharpoons H_2S + PbCl_2.$$

In order to have it proceed from left to right, the active mass of the hydrochloric acid must be large and that of the sulphuretted hydrogen small. This is accomplished by using a considerable quantity of strong acid and allowing the sulphuretted hydrogen to escape from an open vessel, or better by heating. To get the reverse reaction the concentration of the acid must be reduced by neutralization or dilution, and that of the sulphuretted hydrogen increased by passing a steady stream of the gas through the solution. If the lead is to be precipitated completely the conditions must be such that the direct reaction is entirely prevented, *i. e.*, there must be very little acid present. The same considerations apply to other sulphides, such as that of cadmium, and to other precipitates as well.

Effects of Mass Action on Ionization.

Just as the laws of gases have been found to apply to ions in solution as well as to gaseous molecules, as is shown by the osmotic pressures of electrolytes, so the law of mass action is found to apply to the ions in solution; and the effect of mass is the same, whether the dissociation is like that of gases into smaller molecules or in solution of an electrolytic nature into ions.

The addition of an ion in common drives back the dissociation. An illustration of this is found in the fact that while aluminum hydroxide is perceptibly soluble in an excess of ammonia, this solubility is diminished by the presence of ammonium chloride or other ammonium salt. As ammonium hydroxide is slightly dissociated and ammonium chloride almost completely, the mass action of the increased ammonium ions drives back the dissociation of the ammonia, and so readily diminishes the concentration of the hydroxyl ions to such an extent that it is too weak an alkali to dissolve aluminum hydroxide.

The weakening of acetic acid by the addition of an acetate, or the driving back of the dissociation by the addition of an ion in common, can be very strikingly shown by the following experi-

ment: If to a solution of ferric acetate, slightly acid with acetic acid, sulphuretted hydrogen water is added, no black precipitate is found, but only a separation of sulphur due to the reduction of the iron; but if to another portion of the same solution a considerable quantity of sodium acetate is added and then sulphuretted hydrogen water as before, a heavy black precipitate of ferrous sulphide will form immediately, because the mass action of the acetions ($C_2H_3O_2$) has driven back the dissociation of the acetic acid to such an extent that it can no longer dissolve iron sulphide.*

To illustrate this action numerically let:

a = the concentration of H ions in gram molecules per liter.

b = the concentration of $C_2H_3O_2$ ions in gram molecules per liter.

c = the concentration of undissociated acetic acid molecules in gram molecules per liter.

k = a constant.

The law of mass action states that the product of the concentrations of the ionized portion equals that of the undissociated portion times a constant, which is dependent on the nature of the substance, the temperature and the pressure; or using the letters to designate these concentrations $ab = kc$. With acetic acid this would mean that the product of the concentrations of the hydrogen ions and the acetions equalled the concentration of the molecules of acetic acid times k.

Let us suppose that there are present a weight of acetic acid equal to that of two hundred gram molecules at a dilution nearly tenth normal, that is very nearly 6 grams of actual acetic acid per liter. We shall have dissociation to the extent of about 1.5 per cent. or three gram hydrogen ions, three gram acetions and one hundred and ninety-seven gram molecules of acetic acid. Substituting these values for a, b and c, we get

$$3 \times 3 = 0.04568 \times 197.$$

Now if two hundred gram molecules of sodium acetate are added, as this is practically completely dissociated into Na and $C_2H_3O_2$ ions, we are adding two hundred more gram acetions and the situation would be represented as follows:

$$3 \times (200 + 3) = 0.04568 \times 197.$$

* For experiments illustrating ionization mass action, etc., see an article by A. A. Noyes and Blanchard, *Journal of the American Chemical Society*, 22, 727, from which some of the experiments described here are taken.

This is evidently impossible, and contrary to the law of mass action. The addition of the acetions has disturbed the condition of equilibrium and it will only be regained by acetions recombining with hydrogen ions and forming more undissociated molecules of acetic acid until we again have $ab = kc$. This occurs when approximately 2.955 of the three gram ions present have recombined, leaving 0.045 gram hydrogen ions, 200.045 gram acetions and forming 199.955 gram molecules of acetic acid, giving $0.045 \times 200.045 = 0.04568 \times 199.955$ or $9 + = 9 +$ approximately.

By this means the hydrogen ions have been diminished from three grams to 0.045 gram and the percentage of dissociation reduced from 1.5 to 0.0225. So that by the addition of an equal number of molecules of sodium acetate the acetic acid has been made weaker than sulphydric—as shown in the experiment with ferric acetate.

When the addition of a completely ionized salt is made to a substance which is very largely ionized, like sodium chloride to hydrochloric acid, the effect is small. If we consider in the same way, one hundred gram molecules of hydrochloric acid, ninety per cent. ionized we have,

$$(H)90 \times (Cl)90 = 810 \times 10(HCl)$$

$$a \times b = k \times c.$$

When one hundred gram molecules of sodium chloride are added the immediate effect would be,

$$(H)90 \times (Cl)190 = 810 \times 10\ HCl,$$

and to restore equilibrium about eight more gram molecules of hydrochloric acid are formed: then,

$$(H)82 \times (Cl)182 = 810 \times 18.$$

So the grams of hydrogen ions are only reduced from ninety to eighty-two.

If the dilution were greater so that the ionization would be complete, the addition of a solution containing an ion in common would be without effect.

Mass Action on Indicators.

The very confusing action of indicators is explained by the mass action of ions in solution. Only the two indicators most generally used will be discussed. Phenol phthalein is an extremely weak acid, hardly dissociated at all in aqueous solution, the molecule is

colorless, the anion is red. If to water containing a few drops of a very dilute solution of the indicator, a strong base like sodium hydroxide is added, the sodium salt of the weak acid is formed, which is immediately dissociated and an intense red color is produced, due to the ions. When an acid, stronger than that of the indicator is added to the red alkaline solution, the first reaction is with the excess of alkali, giving as the net result undissociated water, as already explained; then the sodium salt of the indicator is affected, yielding the nearly undissociated phenol phthalein; and if the acid used is strong, the change to colorless is instantaneous, due to the driving back of the few dissociated molecules of the phenol phthalein by the hydrogen ions of the acid. To get a sharp change to colorless the concentration of the hydrogen ions from the acid must be sufficient to drive back the dissociation of the indicator by an excedingly small excess of acid. Hence the weaker the acid of the indicator the less the excess of acid required to turn it and so phenol phthalein, which is one of the weakest acids known, serves as an accurate indicator for the weak organic acid as well as for the more highly ionized mineral acids.

In passing from the acid to the alkaline solution (red with phenol phthalein) to get a sharp change in color, it is necessary that the salt formed be unaffected by the hydrolytic action of the water present. It has been stated that water was ionized though to an almost infinitely small extent, but even this has its effect, and when the salt formed is very unstable, as the ammonium salt of phenol phthalein, there is a tendency for a reverse reaction, $NH_4|R + H|OH = NH_4|OH + HR$,* with the formation of undissociated phenol phthalein and no color. This action is entirely overcome by more ammonia, but it prevents a sharp end point with this indicator, when a weak base is used for neutralizing.

Methyl orange is also an acid but much stronger than phenol phthalein, the color of the molecule is red, that of the negative ion yellow. Like other weak organic acids, when this indicator is dissolved in water it is partly dissociated, so that there are present both the red molecules and the yellow ions, which give the so-called neutral color of the indicator. The addition of hydrogen ions immediately drives back this dissociation and gives only the red molecules of the indicator (acid color); while with alkali the

* The phenol phthalein radicle is designated by R.

salt is formed which is dissociated, giving yellow ions (alkaline color).

Let us now compare the action of these two indicators. If to water containing each we add an exceedingly small amount of an acid which is stronger, more ionized than either, the color of the molecule is obtained with each. If we add to each an acid less ionized than methyl orange but more ionized than phenol phthalein, this will be without effect on the methyl orange, but will drive back the dissociation of the phenol phthalein and render it colorless. So there are certain acids which act differently with different indicators and neutrality must be defined by reference to the particular indicator employed. For example, carbonic, sulphurous, sulphydric and boric acids do not affect methyl orange, but react acid with phenol phthalein.

As methyl orange is a stronger acid than phenol phthalein, it gives more stable salts. These are less easily hydrolized, hence this is a better indicator for weak alkalies, like ammonia, than phenol phthalein.

Phosphoric acid affords one of the best illustrations of the action of these indicators; it is a tribasic acid which ionizes strongly into H and H_2PO_4 ions; then the ion H_2PO_4 breaks up to a much smaller extent into H and HPO_4 ions, while the last dissociation of HPO_4 into H and PO_4 ions is too small to be shown accurately by any known indicator. Or, to express this differently, the first hydrogen acts like a strong acid, the second like a weak one, and the third scarcely possesses acid properties. If to a solution of phosphoric acid methyl orange is added and then alkali is run in, the change to yellow occurs when the first hydrogen has been neutralized, for the second is a weaker acid than the indicator and so does not affect it. When phenol phthalein is used the change in color does not take place till the second hydrogen is replaced, as this is sufficiently strong to drive back the ionization of this sparingly dissociated indicator. One indicator marks the change to NaH_2PO_4, the other to Na_2HPO_4. So that the ordinary phosphate of soda, although by constitution an acid salt, gives a strong alkaline reaction with methyl orange.

Solubility Product.

The last application of the law of mass action to ions in solution is the case of a saturated solution. When silver is precipitated as

chloride in an aqueous solution, although silver chloride is one of the most insoluble precipitates, there is still some remaining in solution; and of this silver chloride in solution, a large percentage is dissociated, so we have again for the dissolved portion, the formula $ab = kc$. Here for each precipitate, kc is a constant at a given temperature, its size depending on the solubility of the precipitate. This value was termed by Nernst the solubility product, and here as in the case of an unsaturated solution, we have a state of equilibrium only when $ab = kc$. If ab is less than kc some of the precipitate dissolves. If ab is greater than kc more separates out. In other words as kc is a constant, the equilibrium is adjusted by increase or decrease of the precipitate, instead of by a change in the number of undissociated molecules in solution. Or, the molecules may be regarded as first forming in solution when an ion in common is added; and then, as it is in contact with the precipitate, it can not remain supersaturated and so more precipitate separates out.

So, if to a solution containing a precipitate of silver chloride, an excess of silver nitrate is added, the concentration of the silver ions is increased, the solubility product is exceeded, and silver chloride separates out until ab again equals kc. In this way the addition of ten times the silver ions present reduces the chlorine ions to about one tenth.

This is the explanation of Mulder's end point in the Gay-Lussac titration method, where a portion of the clear supernatant liquid is withdrawn and to one half silver nitrate is added, to the other sodium chloride; when the opalescence in each is equal the end point is obtained.

This cloudiness obtained with silver chloride must be very slight on account of the insolubility of silver chloride. The effect of adding an ion in common is very strikingly shown with silver acetate which is much more soluble. Place one hundred cubic centimeters of a saturated solution of silver acetate in each of three cylinders; to the first add ten cubic centimeters of $4N$ silver nitrate, to the second ten cubic centimeters of $4N$ sodium acetate, to the third several grams of solid sodium nitrate. With the first and second a beautiful crystalline precipitate appears, due to the exceeding of the solubility product by the addition of either silver or acetions; while with the third no precipitate is formed, which shows that the addition of ions not common to the precipitate is without effect.

It is evident that the more soluble the precipitate, the larger will be the solubility product; consequently, the greater must be the excess of reagent added in order to obtain equally complete precipitation. This has been done by chemists for many years as the result of careful quantitative experiment, but the theory of ionization and Nernst's solubility product afford a satisfactory explanation and show why in precipitates like zinc ammonium phosphate, a much greater excess of reagent is required than with others like barium sulphate. Another application of the principle of driving back the ionization or practically decreasing the solubility by the addition of an ion in common with the precipitate, is in the washing of precipitates. Lead sulphate is washed with one per cent. sulphuric acid, as it was found that it was less soluble in this than in pure water, now the reason is found in the influence of the SO_4 ions. There are many other instances, washing cadmium ammonium and other phosphates with water containing ammonium phosphate, calcium oxalate with very dilute ammonium oxalate, etc. The last of the washing solution is removed by a final washing with dilute alcohol in those cases where it can not be volatilized.

Complex Ions.

After having given some of the important applications of ionization and mass action to analytical work it is necessary to give an explanation for the apparent exceptions to the laws.

If to a precipitate of silver cyanide an excess of potassium cyanide is added, or if it is washed with a dilute cyanide solution, instead of obtaining more complete precipitation, the precipitate dissolves. This is due to the formation of a compound, $KAg(CN)_2$, which dissociates into K and $Ag(CN)_2$ ions. A different ion is formed which gives a different set of reactions and we could no more expect the $Ag(CN)_2$ ion to give the reactions of the CN ion than the $PtCl_6$ ion to give those of Cl or the $Fe(CN)_6$ ion those of Fe.

So the apparently abnormal results are caused by a change in the ionization.

During the rest of this article reference will be made to these modern theories only in connection with quantitative precipitations, so for further information the reader must consult the numerous books on physical chemistry among which the following are recommended: Ostwald's Scientific Foundations of Analytical Chemistry, Walker's Introduction to Physical Chemistry, Morgan's Elements of Physical Chemistry.

CHAPTER III.

The Analysis of Magnesium Sulphate and the Determination of Alumina in Alum.

CRYSTALLIZED MAGNESIUM SULPHATE.

When the sample is first received it should be examined to find out whether the crystals have effloresced. If they appear uniform and show no white at the edges, the sample is probably homogeneous and contains the full seven molecules of water of crystallization. If there is any evidence of loss of water the entire sample should be thoroughly mixed and about five grams ground up in an agate or porcelain mortar as quickly as possible and immediately transferred to a small specimen tube which is kept tightly stoppered. When a portion is desired for analysis, weigh the specimen tube containing the average sample; then shake out about a gram into a beaker, taking care that all of the powder removed gets into the beaker, stopper and reweigh the tube. The difference between the weights gives the amount taken for analysis. This is termed weighing by difference.

DETERMINATION OF WATER.

Heat a perfectly clean porcelain crucible and cover over a Bunsen burner until all the moisture is expelled, allow it to cool partially and then place it in a desiccator; cover tightly and allow the cooling to continue in this dry atmosphere till the temperature of the balance room is reached. Then weigh the crucible with its cover and record the weight in a note-book at once. Next shake about a gram of the salt from the specimen tube into the crucible and reweigh the tube. Then weigh the crucible with the salt to see whether the weight checks the sum of the weights of the crucible and the sample taken. There may be a slight loss of water during the operation so that the check is satisfactory when the second weight is either the same as the sum of the two or less by two or three tenths of a milligram. Place the crucible on a pipestem triangle with the cover on and heat it for half an hour with about a four-inch flame from a Bunsen burner, then allow to cool partly, place in a desiccator and when cold weigh quickly. Heat

again for ten minutes at the same temperature, cool and reweigh. If all the water of crystallization has been driven off by the first heating the two weights will be identical. If they differ by more than two tenths of a milligram, the heating must be continued till a constant weight is obtained. Should the weight continue to decrease, even after heating for an hour, loss of sulphuric anhydride, SO_3, is indicated and the determination must be repeated at a lower temperature. The ignition should be made at a moderate red heat, between dull and bright red. With a blast lamp all of the sulphuric anhydride can be driven off. A porcelain crucible is recommended for this determination as it is less likely to be overheated than platinum, because it is a much poorer conductor. A comparison of magnesium sulphate with the other alkaline earth sulphates shows a regular increase of stability with the increase of the atomic weight of the metal.

If the contents of the crucible were allowed to stand in the air moisture would be reabsorbed with an increase in weight.

From the loss in weight the percentage of water is calculated.

Determination of Sulphuric Anhydride.

Weigh out, by difference, into a number two beaker about one gram of the salt (the exact weight being recorded), add about 150 c.c. of hot water and 2–3 c.c. of dilute hydrochloric acid, cover with a watch glass and heat to boiling; while boiling add drop by drop (so as not to cool the solution) from a pipette 20–25 c.c. of a ten per cent. solution of barium chloride, or else dilute 20–25 c.c. of barium chloride solution with water to about 50 c.c., heat to boiling and then add it to the boiling solution of magnesium sulphate. Boil for at least five minutes, while stirring with a thin glass rod to avoid bumping, then allow to settle. If the precipitate does not settle quickly and completely, boil again for several minutes or heat just below boiling for a longer time. Pour the clear supernatant liquid through a nine-centimeter "ashless" filter, which has been moistened with hot water, allowing the precipitate to remain as far as possible in the beaker. Test a few drops of the filtrate in a watch glass or small test-tube with dilute sulphuric acid to make sure that an excess of barium chloride is present. Add 100 c.c. of hot water and one c.c. of dilute hydrochloric acid to the precipitate in the beaker; stir well and then allow the precipitate to settle; pour the liquid through the filter and wash the precipitate twice

more by decantation with hot water alone. Transfer the precipitate to the filter with hot water from a wash bottle, using a rubber-tipped glass rod to detach any particles which adhere to the beaker, and continue the washing with hot water on the paper till the washings show no test for chlorides, when at least three cubic centimeters are tested with silver nitrate solution, or until three cubic centimeters leave no residue when evaporated in platinum.

If convenient, dry the precipitate in an air-bath at about 115° C.; but this is not necessary for this particular precipitate. Place the filter containing the precipitate, either moist or dry, in a clean, weighed platinum crucible; put this on its side on a platinum triangle with the cover in front, so that a current of air shall pass in and over the filter. Then heat the cover by a Bunsen burner so that heat shall be reflected into the crucible and the precipitate dried from the top down. When the water is all expelled, heat the crucible itself gently so as to drive out the volatile matter from the paper without allowing it to take fire. When this is expelled move the flame to directly under the bottom of the crucible and heat, using a large flame, until all the carbon is oxidized. Allow the crucible to cool, and moisten the contents with concentrated nitric acid and reheat till all the acid is expelled. This must be done gradually and cautiously to avoid loss by spattering, and with the crucible vertical and the cover on tight. The object is two-fold, to oxidize any carbon which may remain and to convert any barium sulphide, reduced by the carbon of the paper, to sulphate (this can also be done by dilute sulphuric acid). Cool and weigh, then retreat with nitric or sulphuric acid, expel the acid and weigh again. The two weights should check, if the second exceeds the first by more than two tenths of a milligram, treat again until a constant weight is obtained.

From the weight of barium sulphate calculate the percentage of sulphuric anhydride.

Properties of Barium Sulphate.

A white and very insoluble precipitate of definite composition. If precipitated in a cold or very dilute solution it comes down in such a finely divided state that it invariably runs through the filter paper unless allowed to stand for several hours. When precipitated in a boiling solution and then heated the particles are larger. The theory of the increase in size is as follows: * The

*Oswald, "Scientific Foundations of Analytical Chemistry."

smaller the particle the greater is the ratio of surface to volume; hence the greater proportional contact with the solution. Now every precipitate is soluble to a certain extent, and although this is very small with barium sulphate — about one part in four hundred thousand — still it is perceptible even in the cold and is much increased by heating the solution. When this is done the smallest particles dissolve first, then the solution becomes supersaturated with respect to the larger particles and deposits out barium sulphate on them, so as the boiling continues the larger particles continue to grow at the expense of the smaller. This same action goes on, though very much more slowly, when the precipitate is allowed to stand in contact with the solution in the cold. In order to obtain a successful filtration, this process must proceed till the size of the particles exceeds that of the pores of the filter.

Barium sulphate possesses to a marked degree the property of adsorption, the carrying down of salts from the solution or a sort of condensation of them on its surface; for this reason a very large excess of barium chloride is objectionable, although tending to give more complete precipitation.* The salts carried down in this way do not have their usual solubility and consequently are removed very slowly by washing; so it is always necessary to test the wash-water for chlorides and prove their absence, and not to rely on the fact that a certain volume of water has passed through which would be more than enough to dissolve all of the salts present under ordinary conditions. The other salts likely to be carried down by barium sulphate are alkali and alkaline earth nitrates, chlorides, chlorates and sulphates.

The precipitate is practically insoluble in water, in dilute acetic acid and in hydrochloric acid when present to the extent of one cubic centimeter of dilute acid in one hundred cubic centimeters of water, but it is very appreciably soluble in stronger hydrochloric acid and more soluble in either nitric or sulphuric acids. It is also soluble to some extent in hot acid solutions containing ammonium chloride, ferric chloride, etc., and in solutions of ammonium acetate, citrates and other organic salts.

The tendency of the precipitate to crawl up the sides of the beaker can usually be checked by adding a few drops of hydrochloric acid and boiling. On ignition barium sulphide may be

* See solubility product in Chapter II.

formed which can be reconverted to barium sulphate according to the reactions:

$$BaS + H_2SO_4 = BaSO_4 + H_2S \text{ or}$$
$$3BaS + 8HNO_3 = 3BaSO_4 + 8NO + 4H_2O$$

Silica should be absent, for if not removed it may contaminate the barium sulphate. For the precipitation of barium sulphate in the presence of iron see Chapter VII.

Determination of Magnesia.

Weigh out about a gram of the salt by difference into a small beaker; dissolve it in about fifty c.c. of cold water, add five or six c.c. of dilute hydrochloric acid and then make the solution slightly alkaline with ammonia; if a precipitate of magnesium hydroxide forms dissolve this in dilute hydrochloric acid and again make alkaline with ammonia; repeat this, if necessary, till the solution is perfectly clear when alkaline. Next add slowly drop by drop, from a pipette about twenty-five c.c. of a ten per cent. solution of hydro-di-sodium or hydro-di-ammonium phosphate; stir vigorously, avoid touching the sides of the beaker with the stirring rod, and allow to stand in a cool place for an hour; then add a decided excess of ammonia, about 30 c.c. of ammonia water, specific gravity 0.96, and allow to stand in the cold for several hours longer — over night if convenient.

If the precipitate is perfectly crystalline filter and test a few drops of the filtrate with "magnesia mixture" to make sure that the PO_4 ions are present in excess. It is better to filter and test the filtrate than to withdraw some of the clear liquid with a pipette or tube, as some of the precipitate usually floats. If an excess of the precipitant is present continue the filtration; transfer all of the precipitate to the filter (9 cm.) and wash with very dilute ammonia, one part of strong ammonia water to nine of water (about 2.5 per cent. actual ammonia) till free from chlorides, as shown by no cloudiness being produced when three c.c. of the washings, acidified with nitric acid, are tested with a solution of silver nitrate. Place a large filter on the top of the funnel to keep out dust, put it in an air-bath and dry at from 115°–120° C. When dry separate the precipitate from the paper over black glazed paper and cover the precipate with a watch glass; burn the paper, moistened with nitric acid, in a weighed platinum crucible until perfectly

white, adding more nitric acid if necessary; then add the portion of the precipitate from the paper and ignite, at first gently and then strongly, by the full heat of a burner or with a blast lamp; cool and weigh the magnesium pyrophosphate and calculate the percentage of magnesia.*

Magnesium as well as other phosphates attack platinum in the presence of reducing agents; this is another reason for burning at a low heat and reoxidizing by the addition of nitric acid before heating strongly. Phosphides may be formed even by the reducing gases from the flame penetrating the hot platinum. If the crucible is rough or crystalline after the ignition of a phosphate, it should be scoured with sea sand, as this crystallization gradually penetrates and finally injures the crucible.

Properties of Magnesium Ammonium Phosphate.

Magnesium ammonium phosphate contains six molecules of water of crystallization; it is white and distinctly crystalline; forms slowly when present in small quantity; its separation is accelerated by cold and agitation. If at all flocculent, it is contaminated, most often by magnesium hydroxide or by hydrated silica. The magnesium hydroxide is caused by insufficient ammonium chloride being present to so weaken the ionization of the ammonia that the solubility product of magnesium hydroxide shall no longer be exceeded. This statement is based on recent work † and is accepted by Ostwald in place of the previous theory based on the formation of a complex ion.

If silica is present, it is best to proceed as usual and weigh the magnesium pyrophosphate plus silica; then dissolve out the pyrophosphate by dilute hydrochloric acid, filter and ignite the silica which is insoluble, as it has been dehydrated by the ignition of the precipitate, and deduct the weight from that of impure precipitate.

Magnesium ammonium phosphate is slightly soluble in cold water, one part in 15,000, but very readily soluble in hot water; it is insoluble in dilute ammonia which has an ion in common. If the ammonia is very strong, the precipitate may be too basic, contain more than the right amount of magnesium, hence it is precipitated from a solution which contains but a slight excess of

* For all calculations, the reader is referred to the "Calculations of Analytical Chemistry" by E. H. Miller, which is used as a text-book with these notes.

† Lovén, Z., *Anorganische Chemie*, 11, 404, 1896.

ammonia, to which, after the precipitate has formed, a decided excess of ammonia is added to render the precipitation more complete. In washing, very dilute ammonia should be used as the excess of hydrodisodic phosphate, the usual reagent, is sparingly soluble in strong ammonia. The precipitate is readily soluble in acids. On ignition, the water of crystallization is driven off and also water and ammonia from the molecule giving pyrophosphate.

$$2MgNH_4PO_4.6H_2O + \text{heat} = Mg_2P_2O_7 + 2NH_3 + 13H_2O.$$

It is advisable to dry this particular precipitate before ignition as it retains gases from the paper which leave carbon so intimately mixed with the precipitate that it is very difficult to burn out. The pyrophosphate will stand the heat of a blast lamp without loss. If a loss takes place some other magnesium ammonium phosphate was present and the results are unreliable.

This compound is also used for the determination of phosphoric acid and will be mentioned again under iron ore. In the analysis of crystallized magnesium sulphate the percentages of water, sulphuric anhydride and magnesia should add up to one hundred per cent. whether the sample has lost water or not. Ostwald has recommended calculating the results of analyses to the ions present, for example to Mg and SO_4, instead of to MgO and SO_3, but as the method given here is in general use and is more convenient for metallurgical calculations, the old practice will be adhered to in these notes.

For more information on the phosphates of magnesium see Neubauer, *Journal American Chemical Society*, Vol. 16, p. 290.

POTASSIUM ALUM.

Alums are double sulphates of the alkali metals and of a triad metal and contain twenty-four molecules of water of crystallization; for example, $K_2SO_4.Al_2(SO_4)_3.24H_2O$; $Na_2SO_4.Mn_2(SO_4)_3.24H_2O$; $(NH_4)_2SO_4.Cr_2(SO_4)_3.24H_2O$, etc. The formulæ are often divided and written $KAl(SO_4)_2.12H_2O$, etc. There are many other double sulphates which are not alums, for example Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$.

DETERMINATION OF ALUMINA.

Weigh out either by difference or quickly on a watch glass about one gram of potassium alum; transfer it to a number two beaker and dissolve in about 100 c.c. of hot water and five or six c.c. of

concentrated hydrochloric acid; make slightly alkaline with ammonia avoiding more than enough to make the solution smell faintly of ammonia while hot. If too much be added, neutralize it by dilute hydrochloric acid. Heat to boiling, while stirring continually to avoid "bumping," and allow the gelatinous precipitate of aluminum hydroxide to settle; decant the clear solution through the filter and wash the precipitate four or five times with 100 c.c. of boiling water, stirring up thoroughly each time and decanting through the filter; transfer to the paper with hot water and wash with hot water till the washings give no test for chlorides or sulphates.

This precipitate is extremely hard to wash on account of its gelatinous nature and must neither be allowed to stand before filtration, as it becomes insoluble and adheres to the beaker, nor should it be allowed to stand over night on the filter unless completely washed, for it contracts on drying, leaving cracks through which all the wash-water passes, making it impossible to remove the salts by washing.

It is unnecessary to separate this precipitate from the paper and no especial precautions are required in igniting; as the alumina is neither easily reduced nor volatile if the chlorides have been removed. Weigh the alumina and calculate the percentage.

Properties of Aluminum Hydroxide.

Aluminum hydroxide when freshly precipitated is very readily soluble in acids, both strong and weak, but on standing it becomes difficultly soluble even in hydrochloric acid; it is also soluble in caustic alkalies and to a slight extent in ammonia. In the plan just given the solvent action of the slight excess of ammonia is so weakened by the mass-action of the ammonium ions from the ammonium chloride, that it is no longer a sufficiently strong alkali to dissolve aluminum hydroxide. The action of strong alkali in dissolving alumina is to make this very weak base take the part of an acid so that the cation Al''' is changed to an anion $\bar{A}\bar{l}\bar{O}_3$.

A difficulty which may possibly arise is contamination by basic sulphates of aluminum and which may be most readily avoided by pouring the aluminum solution into an excess of ammonia.

The precipitate is in general likely to be contaminated by those metals whose hydroxides are precipitated in a weakly alkaline solution such as iron, manganese, chromium; also magnesium, zinc,

cobalt, nickel and copper; also phosphates and arsenates, calcium carbonate and hydrated silica. It is because there are so many possible contaminants, whose separation is difficult, that alumina is often determined by difference; that is, the total weight of the precipitate is taken and deductions made for the impurities from the results of separate determinations.

Organic acids, such as tartaric and citric, and also sugar and glycerin, prevent the precipitation of the hydroxide. The alumina obtained after strong ignition is insoluble in acids, but can be obtained as a readily soluble aluminate by fusing with alkalies, either caustic or carbonate.

For the analysis of bauxite and of aluminum alloys, see Handy, *Journal American Chemical Society*, 18, 766, 1896; Phillips and Hancock, same, 20, 207, and Lunge, "Chemisch-technische Untersuchungs Methoden," Vol. II., p. 349 and seq.

CHAPTER IV.

Coal Analysis.

SAMPLING.

In all analytical work it is of the utmost importance that the small portion taken for analysis accurately represents the average composition of the lot whose analysis is desired; otherwise the analysis is worthless and misleading for practical purposes. This is especially true with coal, where not only may the sulphur and ash be irregularly distributed, but the amount of moisture may vary from day to day, depending on the weather; if exposed to rain or sunshine the percentage of water differs and for this reason, a carload may have a different composition when it arrives at its destination from that which it possessed when mined. These discordant results should however agree, when calculated to the dry basis if the sampling has been done correctly.

The sample received by the chemist should be at least 5 pounds. This is to be crushed up immediately, so as to avoid any loss of water and quartered, until about a half pound is obtained; this is then ground to 40-mesh and divided in half, and one half immediately sealed as a reserve sample in case of dispute or accident. The remaining sample is weighed and air dried at 80–90°C., allowed to cool in the air, and the amount of moisture determined. It is mixed up thoroughly on glazed paper and quartered down to about twenty grams which are ground fine (100-mesh) and used for the analysis. The object of this treatment is to obtain the water in the sample as received before it has a chance to dry out in the warm atmosphere of a laboratory, and to obtain an air-dried average sample, which is not likely to lose or absorb moisture, from which to weigh out portions for analysis. It is to be borne in mind that water is still present in the coal and that in calculating the analytical results to the original sample the loss in weight in air drying must be considered. This is most readily accomplished, if we regard the original sample as made up of a certain weight of air-dried sample plus a certain weight of water and correct our percentages accordingly.

These principles apply with equal or even greater force to large lots of ore, matte, slag, etc.

Proximate Analysis.

Moisture.—Dry one gram of the coal in an air-bath in an open porcelain or platinum crucible for one hour at a temperature between 104°–107°C. Cool in a desiccator and weigh covered. The loss in weight is moisture. This apparently simple determination is very difficult if extraordinary accuracy is required, as water may be lost during the fine grinding of the sample, and also because all the water may not be given off in an hour at the temperature given. It is however the standard method and is sufficiently accurate for technical purposes; the error being probably less than that of sampling.

Volatile Combustible Matter. — Place one gram of the air-dried sample in a platinum crucible, weighing 20–30 grams, and having a well-fitting cover. Heat over the full flame of a Bunser burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom 6–8 cm. above the top of the burner. The flame should be 25 cm. high, and the determination made in a place free from draughts. The upper surface of the cover should burn clean but the under surface remain covered with carbon. To find the volatile combustible matter subtract the percentage of moisture from the percentage of loss found here.

This method is evidently arbitrary and open to the objections of the possibility of oxidation on one hand and incomplete expulsion of the volatile matter on the other; but by following it carefully the results possess uniformity, if not scientific accuracy, and it is the method in general use. The loss due to oxidation, particularly with coke, can be diminished by using a much larger sample, say 10 grams. With coke the last of the volatile matter should be removed by a couple of minutes over a blast lamp.

Ash. — Burn the portion of powdered coal used for the determination of moisture, at first over a very low flame, with the crucible open and inclined, till free from carbon. This sample can be burned much more quickly than the dense carbon or coke left from the determination of the volatile combustible matter.

Fixed carbon is found by difference. Either subtract the percentage of ash from the percentage of coke (residue left when water and volatile matter are driven off) or subtract the sum of the other percentages from 100.

Determination of Sulphur.

Sulphur exists in coal in three conditions — as sulphide, FeS_2, as alkaline earth sulphate, $CaSO_4$, and as an organic compound. On heating FeS_2, out of contact with the air, Fe_7S_8 is usually left behind. So in the determination of the volatile combustible matter, the sulphur present as an organic compound (if any) and nearly one half the sulphur present as pyrites is driven off. And in burning off the fixed carbon the Fe_7S_8 is changed to Fe_2O_3 with a loss of the sulphur remaining from the pyrites. The ash contains the sulphate sulphur.

It was formerly customary to consider all the sulphur was present as FeS_2, and that one half of this went off with the volatile matter and the second half with the fixed carbon; so that one half the percentage of sulphur was subtracted from each of these percentages to make the results add up to 100 per cent. Although this method is still in use it is evidently not strictly in accordance with the facts and, as it is never correct to state more in a report than is actually known, it is preferable to report the percentage of sulphur separately and let the sum of the other determinations add up to 100 per cent.

When the sulphur in the ash is desired separately from the total sulphur, a large portion, 10–12 grams, of the coal is burned and the sulphur determined in the ash by methods similar to those which will be given under iron ore and slag analysis.

Total Sulphur. Eschka Method Modified.—One gram of the finely pulverized coal is mixed with one gram of light magnesium oxide and 0.5 gram of anhydrous sodium carbonate in a platinum dish having a capacity of 75–100 c.c. or a Meissen porcelain crucible, and heated with an alcohol lamp. When great accuracy is not required a gas burner may be used, the dish being protected, as far as possible, from the products of combustion, which contain sulphur. The mixture is stirred frequently with a stout platinum wire or glass rod and the heat applied gradually, especially with soft coals, until strong glowing has ceased; then the heat is increased until in fifteen minutes the bottom of the dish is at a low red heat, which is maintained until all the carbon is burned out. The residue which should be nearly white and porous is transferred to a No. 2 beaker with about 50 c.c. of water, 15 c.c. of bromine water are added and the whole boiled for at least 5 minutes, allowed to settle

and decanted through a filter and boiled, a second and third time with 30 c.c. of water and then washed very thoroughly with hot water. The filtrate is acidified with hydrochloric acid so as to have an excess of about 1 c.c. and boiled to expel any free bromine. Then to the hot solution barium chloride (10 per cent. solution) is added drop by drop, until 10 c.c. have been added and the solution boiled or heated on a water-bath until the precipitate settles quickly, filtered and treated as already described. From the weight of $BaSO_4$ the percentage of sulphur is calculated.

The treatment with magnesium oxide, sodium carbonate and air, oxidizes the sulphur present to sulphurous and sulphuric anhydrides which combine with the bases present. The mass must not fuse as it would then be much more difficult to oxidize and as the silica from the ash would thereby be rendered soluble. It is for these reasons that magnesia is selected on account of its bulk and infusibility.

When the mass is leached the soluble sulphites and sulphates pass into solution, together with the excess of sodium carbonate, while the bulk of the magnesia and the ash remain insoluble. It is at this point that an important reaction takes place, the ash may contain calcium sulphate which is acted on by the excess of sodium carbonate, giving calcium carbonate which remains behind and sodium sulphate which passes into solution, and by this means the total sulphur is obtained in the filtrate.

The bromine, in the alkaline solution, oxidizes any sulphites present to sulphates. It is important to acidify after, not before filtering, as the latter would take magnesia into solution ; also alkaline earth carbonates which would immediately react, giving insoluble sulphates and so cause low results.

The solution after filtration is made but slightly acid and a liberal excess of barium chloride is added to get complete precipitation of all the sulphur as barium sulphate.

This method is most satisfactory, but for very accurate results certain precautions not already mentioned must be observed:

The magnesia and the sodium carbonate must be tested for sulphur as they often contain small quantities which are enough to interfere with the accuracy of the determination. If present the sulphur should be determined in 20-gram lots and the percentage marked on the reagent bottles and deducted from the results.

The residue after leaching may in some cases contain sulphur,

if much calcium sulphate should be present and the excess of sodium carbonate be insufficient to convert it. In such a case the residue is treated with hydrochloric acid and filtered, the filtrate neutralized closely and any sulphate precipitated as barium sulphate and added to that obtained in the main portion.

The original barium sulphate may be contaminated by silica. If the heat has been too high or the ash very siliceous, some sodium silicate may be formed, dissolved and hydrated silica be carried down with the barium sulphate. To avoid this, evaporate the solution to dryness after the bromine is boiled out and heat at 120° C. until the hydrochloric acid is driven off to render the silica insoluble; then take up with hydrochloric acid and water, filter and determine the sulphur as usual in the filtrate.

For further information see Report to American Chemical Society, *Jour. Amer. Chem. Soc.*, 21, 1119, and Stoddart on the "Determination of Sulphur in Coal," *l. c.*, 24, 852.

CHAPTER V.

Ferric Ammonium Alum.

DETERMINATION OF FERRIC OXIDE GRAVIMETRICALLY.

By Ignition.—As this compound contains only ferric sulphate, ammonium sulphate and water, simple ignition will drive off everything except ferric oxide. So the percentage can easily be found by igniting a gram in a weighed platinum crucible to constant weight. In order to decompose the ferric sulphate more readily than by heat alone, a little ammonium carbonate is often added and then the residue reignited. The reaction is $Fe_2(SO_4)_3 + 3(NH_4)_2CO_3 = Fe_2O_3 + 3(NH_4)_2SO_4 + 3CO_2$.

The application of this method is extremely limited, and even with this alum, if impurities were present they would contaminate the ferric oxide.

By Precipitation with Ammonia.—Dissolve about a gram of the alum in hot water and a few c.c. of hydrochloric acid, heat to boiling and add at once, but carefully to avoid spattering, an excess of ammonia; heat till the precipitate collects well; decant through a filter and wash by decantation and then on the filter with hot water, till free from chlorides. Transfer the paper and precipitate to a weighed platinum crucible and moisten with strong nitric acid; ignite gently till the water and volatile matter have been expelled; then allow to cool, moisten again with nitric acid and burn out the carbon; ignite and weigh; check by moistening once more with nitric acid and reweighing; calculate the percentage of Fe_2O_3.

In this particular analysis, the only difficulty is in avoiding any reduction of the ferric oxide by the paper, for if once reduced to the magnetic oxide, reoxidation is difficult. In general, however, when iron is precipitated by ammonia certain precautions must be observed.

The iron must all be in the ferric condition as ferrous iron is not completely precipitated by ammonia, but a white precipitate of ferrous hydroxide is formed which immediately turns green; with mixtures of ferrous and ferric iron, green, black or brownish precipitates are formed.

When the higher groups have been previously removed by sulphuretted hydrogen, the iron is conveniently reoxidized by nitric acid or hydrogen peroxide.

In the alum we did not boil out the excess of ammonia, but if there are present elements of the fifth periodic group, phosphorus, arsenic, vanadium, etc., the excess of ammonia must be expelled in order to obtain complete precipitation of the iron. Under these conditions phosphorus, vanadium, arsenic and antimony are carried down as well, in combination with the iron as $FePO_4$, etc.

Should we wish to use the filtrate for the determination of sulphur, we must proceed differently, as there is danger that the ferric hydroxide may be contaminated by a basic ferric sulphate; although this would not cause any inaccuracy in the iron determination, as the sulphuric anhydride would be driven off on strong ignition. In this case pour the acid ferric solution into a large beaker containing 200 c.c. of water and an excess of ammonia over that required to precipitate the iron and neutralize the acid present. In this way the ammonia will always be in excess and the danger of forming basic sulphates near the neutral point is avoided.

The presence of ammonium chloride, or other ammonium salts, favors the separation of the hydroxide and prevents its becoming colloidal. They must be washed out, however, to prevent loss of ferric chloride on ignition. Ferric hydroxide is soluble in acids both weak and strong, and insoluble in alkalies. Its precipitation is prevented by citric acid, tartaric acid and other organic substances such as sugar, glycerine, etc., because they form complex ions containing Fe, which no longer give the reaction of the ferric ion.

This precipitate is very likely to be contaminated not only by sulphates, phosphates, arsenates, etc., as already mentioned, but also by hydrated silica and by the hydroxides of aluminum, chromium, manganese, and also by those of magnesium, cobalt, nickel, zinc and copper. Of the latter, magnesium and zinc can be removed by reprecipitation, but with copper, nickel and cobalt the separation is not easy. As these elements, or some of them, are always present in iron ores, the gravimetric method is seldom used except to throw down together hydroxides of aluminum and iron with phosphoric acid.

One other property of ferric salts should be mentioned, the effect of water on them. Ferric iron is a very weak base and when com-

bined with a weak acid in a neutral solution it is easily hydrolysed, especially on heating, with the formation of basic ferric salts. It is for this reason that hydrochloric acid is added to the alum when it is dissolved, to give a clear solution, as well as to form ammonium chloride.

Determination of Ferric Oxide Volumetrically. By Potassium Permanganate.

A standard solution of potassium permanganate is required which should be approximately $N/10$. Dissolve 6.4 grams of pure potassium permanganate in about 400 c.c. of water, warm slightly to assist the solution, then filter through a layer of asbestos supported by a cone or porcelain plate in a large funnel or a Gooch crucible; allow the solution to run into a clean dry liter flask; wash the residue on the asbestos, hydrated manganese dioxide, with water and then dilute the permanganate solution in the flask to the delivery mark with cold distilled water (if the solution is still warm allow it to cool to the temperature for which the flask was graduated and make up the contraction by more water). Pour the contents into a clean dark glass bottle, with a well-fitting ground-glass stopper; fill the liter flask again with water to the delivery mark and add this also to the bottle containing the permanganate solution. Mix by very thorough shaking and allow to stand several hours before standardizing.

The warming and removal of the dioxide, which is formed by organic dust, etc., by filtration, gives a solution which retains its strength better than if this process goes on gradually in the bottle.

The solution must be filtered through asbestos for it is decomposed by filter paper, rubber and other organic materials. If an old permanganate solution can be obtained, it will remain more constant and so require standardizing less frequently than a freshly made solution. The solution obtained will be nearly $N/10$, but its strength must be determined by experiments, and the results should not differ from each other by more than one in the fifth place; *i. e.*, 0.00561 and 0.00562 is the greatest error allowable in duplicates for the value of 1 c.c. in terms of iron. Many methods of standardizing have been proposed * of which three will be mentioned here.

* Thiele and Deckert, *Z. Angewandte Chemie*, XIV., 1233, 1901; Dupré and Muller, *Z. Angewandte Chemie*, XV., 1244, 1902; Rust, *Z. Analytische Chemie*, 41, 606, 1902.

Iron Wire Method. — Take a spool of soft iron wire, such as is used by florists, and remove any superficial layer of oxide by emery paper; this will then be very close to 99.7 per cent. iron. The actual iron contents can be determined best by finding the percentage of impurities and subtracting it from one hundred per cent. Weigh out two portions of about 0.2 gram each, weighed exactly of course, but not exactly the same weight; place these in two 250 c.c Erlenmeyer flasks, add a few grams of sodium bicarbonate to each and then about 100 c.c. of dilute sulphuric acid (one part of concentrated acid to five of water) and immediately close each with a rubber stopper, through which passes a bent glass tube reaching to the bottom of a beaker of distilled water. Heat both the flask and the beaker of water till the wire has completely dissolved,* best on a hot plate heated by gas, then turn off the heat and allow the water in the beaker to be drawn back so that it almost fills the Erlenmeyer flask.

The sodium bicarbonate is added so that carbon dioxide shall be liberated by the action of the sulphuric acid which will replace the air in the flask. The water seal prevents any contact with the air during solution so that the iron dissolves, according to the reaction $Fe + H_2SO_4 = FeSO_4 + H_2$, entirely to ferrous sulphate, while the hydrogen bubbles up through the water in the beaker. The water in the beaker is heated also to expel the air dissolved in it, so that it shall be free from oxygen when it comes in contact with the ferrous solution.

There is one situation to be guarded against, if attention is not given and the water is not allowed to run over soon after all the iron is dissolved, the water will keep on evaporating from the flask and the sulphuric acid become concentrated; then, when the hot water comes in contact with the concentrated sulphuric acid an explosion ensues which destroys the determination and may be dangerous to the operator. This is easily avoided by preventing the concentration of the acid. While the iron is dissolving get ready a fifty c.c. burette, which has been found to be accurately graduated, fill it with water and allow it to run out to see whether drops adhere to the sides; if they do clean it thoroughly by alcohol or ether to remove the grease, or by potassium dichromate and sulphuric acid; then rinse out with water and dry by alcohol

* The action can be hastened by a drop of hydrochloroplatinic acid solution.

or else add ten c.c. of the permanganate solution, shake thoroughly and allow the solution to run out through the stopcock; then repeat this again and again, so that the burette is wet with a solution so nearly the strength of that to be used that no perceptible dilution results when the burette is filled with the permanganate solution.

Fill the burette and adjust to the zero mark, reading the top of the meniscus with this dark solution.

Pour the ferrous sulphate solution into a large beaker, and rinse out the Erlenmeyer flask with cold distilled water, then dilute with cold distilled water to about six hundred c.c. and the solution is ready for titration. Run in the permanganate solution, a few drops at a time, till the pink color disappears slowly, then drop by drop till finally one drop gives a pink tinge to the whole solution, which is slight but perceptible and permanent. Then wait for two minutes for the solution on the sides of the burette to run down and for the pink color to disappear, if the end has not been reached, and read the volume of permanganate used.

Titrate the second portion of iron wire the same way and compare the results. The reaction is

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

If the solution should turn brown it is a sign that the manganese is not being reduced completely to manganous sulphate and more sulphuric acid must be added at once.

Standardizing by Mohr's Salt.— Here the iron is already in the ferrous condition, and as the molecular weight is large — about seven times that of the iron atom — any error in weighing, etc., is only one seventh of what it would be when metallic iron is used. The disadvantage is the possibility that some water of crystallization has been lost so that the salt is not exactly $(NH_4)_2SO_4.FeSO_4.6H_2O$. Select crystals which have no white appearance at the edges and weigh out quickly two portions of 1–1.5 grams each; place them in large beakers, add water and ten c.c. of concentrated sulphuric acid, and when the crystals have dissolved, dilute to about six hundred c.c., add more sulphuric acid and titrate as already described. Calculate the results and compare them with those obtained with the wire. Some prefer making up a standard solution of the ferrous salt and measuring this out from a second

burette, but separate weighings of different weights are preferable for beginners because if there should be any error in the weight of the salt taken the titration results would check though the standard would be wrong and the error might not be discovered till much later.

Oxalic acid or *oxalates* may be used for standardizing. The reaction is

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O,$$

which takes place best in a warm solution acid with sulphuric acid. The temperature should be 50–60° C. and ten grams of manganous sulphate should be added to make the reaction take place rapidly; the end point is the same permanent pink, but, as the oxidation is less prompt than with iron, some time must be allowed, several minutes, to oxidize the last traces. Here if we weigh out crystallized oxalic acid we have the doubt as to whether it really is $H_2C_2O_4.2H_2O$. If the water of crystallization is right the method is excellent. $(NH_4)_2C_2O_4.H_2O$, $KHC_2O_4.H_2C_2O_4.2H_2O$ are salts frequently used; also lead oxalate, PbC_2O_4, which on account of the high atomic weight of lead and the absence of water of crystallization presents theoretical advantages.

Determination in Ferric Alum.—As the iron in the alum is in the ferric condition it must be reduced before titration. This is done most conveniently by passing the solution, acidified with sulphuric acid, through a Jones reductor. The simplest form of this apparatus consists of a piece of glass tubing about 2 cm. in diameter and at least 40 cm. long, which is widened at the top like a funnel and drawn out at the bottom like the stem of a funnel, so that it will pass easily through the hole in a rubber stopper. A perforated platinum cone or disc of platinum is placed at the bottom of the wider portion and on this a plug of glass wool, about 8 mm. thick, covered by a thin layer of asbestos fiber; then the tube is filled nearly to the top with granulated zinc, 20–30 mesh — that which will pass through a 20-mesh sieve but not through a 30, is the best size.

The zinc is amalgamated as follows: * Dissolve 5 grams of mercury in 25 c.c. of nitric acid, 1.2 sp. gr., dilute to 250 c.c. and pour into a large flask; to this add 500 grams of granulated zinc,

* Blair, "Chemical Analysis of Iron," p. 95, etc.

shake thoroughly for two minutes and then pour off the solution; wash the zinc repeatedly with water and fill the reductor with it. Weigh out two portions of ferric ammonium alum, about 2 grams each, dissolve these in about 100 c.c. of water and about 50 c.c. of dilute sulphuric acid. Place the reductor through the rubber stopper of a stout Erlenmeyer flask which is connected by a side tube with the suction. Pour the solution into the reductor and turn on the suction gently, adding the rest of the solution so that the zinc is always covered. As the ferric solution passes through, add 200 c.c. of water containing 10 c.c. of concentrated sulphuric acid and then follow this with 100 c.c. of water.

The solution, assuming its volume not to exceed 200 c.c., should require at least four minutes to pass through the reductor. The titration can be made directly in the reductor flask after dilution if necessary, as already described. The duplicates should agree closely and check the gravimetric results when calculated to percentage of Fe_2O_3. (The permanganate standard is in terms of Fe.)

The length of the column of zinc should be at least 35 cm., and when freshly filled or after standing some time it should be washed with dilute sulphuric acid. Then a second lot of dilute sulphuric acid should be run through and this titrated with permanganate. If more than a drop is required to color the solution, the amount must be determined and subtracted from the subsequent titrations. This is due to the iron which is usually present in zinc and whose solution may not have been entirely prevented by the amalgamation.

If air is allowed to pass through the reductor after an acid solution and then followed by acid again, hydrogen peroxide may be formed, which uses up permanganate according to the reaction.

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = 5O_2 + K_2SO_4 + 2MnSO_4 + 8H_2O,$$

and so gives too high results.

This method can also be applied in standardizing. Dissolve the iron wire by dilute sulphuric acid in a beaker in the presence of air, then run the solution of ferric and ferrous sulphates through the reductor and titrate.

The permanganate titration depends on the oxidation of the iron present from the ferrous to the ferric condition by a solution of known oxidizing power, hence any other oxidizing or reducing agents which would affect permanganate must be absent. Sulphuric is the best acid to use, but hydrochloric is permissible under carefully regulated conditions.

By Potassium Dichromate.

Make up a solution of potassium dichromate containing 4.9 grams per liter and standardize it as follows: Weigh out at least two portions of clean iron wire about 0.2 gram each, and dissolve them in small beakers in about 20 c.c. of hydrochloric acid 1.1 sp. gr.; rinse down the cover and sides of the breaker and while still hot add drop by drop from a pipette a very dilute and strongly acid solution of stannous chloride until the solution becomes colorless; then dilute to about 50 c.c. and add at once 10 c.c. of a saturated solution of mercuric chloride, which should give a white silky precipitate of mercurous chloride; pour this solution into distilled water containing 20 c.c. of concentrated hydrochloric acid and dilute to about 600 c.c. Place on a porcelain tile or plate some drops of a very dilute and freshly prepared solution of potassium ferricyanide. Run in the dichromate solution until nearly the calculated quantity has been added, then after stirring, remove a drop and place it in contact with a drop of ferricyanide on the plate. A blue color will result due to the reaction between the ferricyanide and the ferrous iron still present; continue adding dichromate from the burette until no blue coloration is produced with a drop of the indicator. Treat the second portion in the same way and calculate the standard of the solution in terms of iron. The results should agree as closely as in the permanganate titration. The reaction of titration is:

$$6FeCl_2 + K_2C_2O_7 + 14HCl = 6FeCl_3 + 2KCl + 2CrCl_3 + 7H_2O$$

and for the blue color,

$$3FeCl_2 + 2K_3Fe(CN)_6 = Fe_3(Fe(CN)_6)_2 + 6KCl.$$

The special precautions to be observed are: To keep the solution concentrated, hot and strongly acid when reducing by stannous chloride and to avoid an excess of more than one drop. If the solution is cold, dilute or insufficient hydrochloric acid is present, the reduction is slow and an excess of stannous chloride is added before the solution becomes colorless; then when the mercuric chloride is added a black precipitate of finely divided mercury results, which destroys the determination as it is likely to be oxidized by the potassium dichromate.

The reactions are: $Fe + 2HCl = FeCl_2 + H_2$; $2FeCl_2 + 2HCl + O$ (from the air) $= 2FeCl_3 + H_2O$; $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$ and

with the excess of stannous chloride, $SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$. If the excess of stannous chloride is too great we get $SnCl_2 + Hg_2Cl_2 = SnCl_4 + 2Hg$.

The 10 c.c. of mercuric chloride solution should be added at once to get it in excess as regards the stannous chloride as quickly as possible and so avoid the last reaction. The indicator must be free from ferricyanide, for if this is present we get a blue with the ferric salt as well, and so no end point. It should for this reason be made up by dissolving a crystal the size of a pin head in water in a small watch glass; if more concentrated, the brown coloration due to ferric ferricyanide may mask the blue. When properly carried out the end point is extremely sensitive.

To determine the iron in the alum, weigh out two portions of about 2 grams each and dissolve in hydrochloric acid 1 : 1 using 30–40 c.c. and heating; then reduce by stannous chloride, using more, of course, than with the wire, and carry out the operation just as in standardizing.

This method has many advantages: first, it is extremely accurate; second, it can be done, and is best done, in a hydrochloric acid solution which is the best solvent for iron in ores; third, the reduction by stannous chloride is very rapid and at the same time does not reduce the titanic chloride often present from magnetites, while zinc reduces this to $TiCl_3$, which is reoxidized by permanganate giving too high results.

The disadvantage is the outside indicator which is tiresome and may cause inaccuracy when too many drops are removed. It is evident that this solution may be standardized by Mohr's salt but not by oxalic acid or oxalates as there would be no end point.

GEOLOGY OF THE SAN PEDRO DISTRICT, SAN LUIS POTOSI, MEXICO.

By GEORGE IRVING FINLAY, PH.D.

In June and July, 1903, the writer, at the invitation of Mr. George F. Laird, director of the mines of the Victoria y Anexas Company at San Pedro, in the State of San Luis Potosi, Mexico, and of Mr. W. G. Brown, of the Compania Metallurgica, in the city of San Luis Potosi, spent a month in studying the geology of the San Pedro district. He wishes to acknowledge his great indebtedness to these gentlemen, and to call attention particularly to the paper by Mr. Laird in the 1903 volume of the American Institute of Mining Engineers, in which the conditions at the San Pedro mines are outlined and the course of the development work described. The present contribution is intended to supplement that paper with an account of the geological relations of the ore bodies.

The town of San Pedro lies 15 miles to the east of San Luis Potosi, Mexico. The mines, which have been worked at San Pedro since 1573, are the second largest in the State. The total output is not less than $750,000,000. They produce gold, principally, with lesser amounts of silver, and associated lead and iron. The mineralized district, surrounding the town, is of small extent, embracing not over two square miles.

San Luis Potosi, the capital of the State of that name, lies near the eastern border of a very level plain 20 miles wide. Its elevation is 6,118 feet above the sea. To the east and west of the city are extensive mountain ranges. San Pedro is situated in a narrow gulch behind the first foothills of the eastern range, a thousand feet higher. The mountain slopes coming down to the town on all sides are steep, 20 to 30 degrees. The relief is great. Rain very rarely falls at San Pedro. The dry stream-ways wind past the town 900 feet below the surrounding mountain tops. All the principal mines lie to the north and west in San Pedro and Popolo hills. Bounding the view to the south of San Pedro is the flat-topped hill of Las Catitas. A controlling influence on the topography has been exercised by the flow of rhyolite, which is seen lying as a cap on this mountain over the country rock, a massive limestone. The same rhyolite appears on the tops of the more distant hills in all directions. Small remnants of the original flow

show at present in buttes and sloping mesas. Below the level of the igneous cap the limestone has everywhere been cut into symmetrical, evenly-rounded slopes between sharp gulches.

General Geology.— The country rock in the San Pedro district is limestone, capped by rhyolite over hundreds of square miles and underlain, near the town, for a very short distance by andesite. No dyke rocks have been noted. The limestone is a dense even-grained greenish or bluish rock, homogeneous and regularly

View of San Pedro, the Guadelupe Patio, and manager's residence.

bedded. It may at times be almost black and is again reddish from contained iron. It is almost free from effects of weathering except for shallow incrustations of "caliche," which are due to natural air slacking and recementation. The single strata are often three feet thick with thinner bands not more than a few inches through. Shaly layers are of rare occurrence in a series where between three and four thousand feet are exposed. The strike varies over wide distances from N. 25° E. to N. 25° W. The dips, which are usually high and often vertical, vary much from point to point. The whole series has been tilted and folded as anticlines and synclines with sharp buckling of certain strata into Z folds

between others, above and below, not greatly disturbed. These folds are not usually accompanied by faulting, but the large flexure on the road coming into San Pedro from the southwest shows a displacement where it pinches, of twenty feet. Slips along the bedding planes of a few inches are common, as are lesser dislocations across the planes of stratification, but large faults are rare in the San Pedro district. The limestone layers very often contain disconnected bands of chert, a foot or more in length by an inch or two in width. These have been bent and broken. Rounded siliceous inclusions a foot in diameter are found more rarely in the dense limestone. The rock shows no effects of metamorphism, and it does not contain fossils to the writer's knowledge, in the immediate vicinity of San Pedro. Lamellibranchs and other fossils of Cretaceous age are found, however, in the limestone at Mesa Verde, 30 miles to the northwest, in beds which are apparently in the same series with the San Pedro rocks.

Over the limestone on the highest hills are found remnants of a very extensive sheet of rhyolite. The original thickness of this extrusive flow is estimated at from 100 to 150 feet. The remnant which has not been removed by erosion, averages 60 feet in thickness. The surface now presented in the lower planes of the rhyolite caps is uneven and gently rolling. The rock sank several hundred feet in flowing down to the plain on which San Luis Potosi is built. It may be traced across the level floor of the valley until it appears to the west of that city where it has been employed in the construction of the great reservoir for irrigation purposes. The rhyolite usually stands in cliffs which are made up of the rude prisms, three or four feet in diameter, blocked out by columnar jointing. In field habit the massive rock varies but slightly from point to point. It is medium grained and light reddish-brown in color. In the hand specimen crystals of quartz and glassy feldspar appear in abundance through a siliceous ground-mass. Many of the feldspar crystals, when examined with a hand lens, show polysynthetic twinning. The rock appears to the unaided eye to be without dark silicates. When seen under the microscope the phenocrysts of feldspar are found by their extinctions to be usually an acid plagioclase. A very little orthoclase is present. Quartz, at times in corroded crystals, is again bounded by prismatic planes giving six-sided sections. The rock is very rich in magnetite. Large grains of the mineral have

gone over to hematite with which the ground-mass is deeply stained.

The rhyolite frequently shows a tendency toward a glassy habit, and there is evidence of successive flows over short distances where part of the magma has been quickly chilled as a glass and covered by the main body of the flow. This phenomenon may be observed on the northern slope of Populo Hill near the summit. The layer of obsidian is about five feet in thickness. It outcrops on Las

Caved territory above Gogarron, showing on the left side, surface slopes in limestone.

Catitas and again along the road to the southwest of San Pedro a mile and a half from the town. In the hand specimen the rock appears as a black glass abundantly provided with spherulites an eighth of an inch or less in diameter. The vitreous ground-mass which shows lines of flow structure under the microscope is deeply stained with limonite. It contains a few small plagioclase crystals and occasional splintery pieces of quartz.

In the immediate vicinity of San Pedro, but so far as observed at no other locality, the limestone country rock is underlain by andesite. Surface outcrops of this igneous body, which is entirely surrounded by limestone, appear over a square mile at various

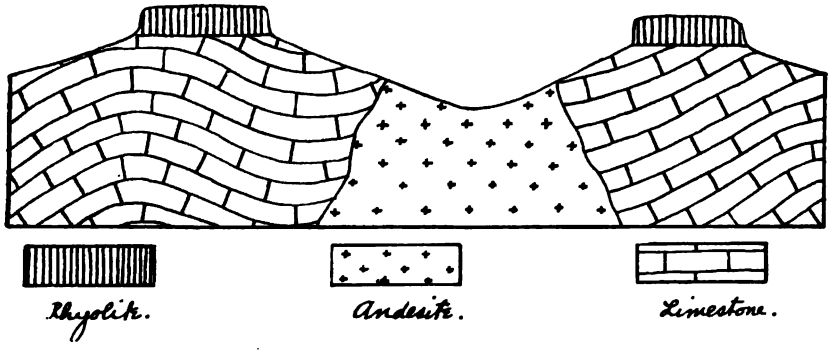
points north and east of the town. The andesite is immediately below the surface on the hill of Las Catitas where along the northern slope a cover of limestone but a few feet in thickness lies between it and the rhyolite above.

When undecomposed the andesite is a coarsely porphyritic drab-colored rock. Grayish crystals of plagioclase a quarter of an inch or less in diameter, with smaller, six-sided pieces of mica are the most prominent phenocrysts visible without the aid of the microscope, although cubes of secondary pyrite are often found. For hundreds of feet below the surface the andesite is much decomposed and kaolinized. The feldspar is the first mineral to go. With the ground-mass it forms a soft, clayey aggregate, usually stained red with iron, around the more unyielding, scattered crystals of mica. The rock may readily be distinguished from the rhyolite in the hand specimen by the absence of quartz and by its content of mica. Joints are numerous all through the mass of the andesite. They have carried surface waters, which have decomposed the wall-rock to a depth of over 900 feet. In some of the mines acicular crystals an inch or less in length are found in aggregates hanging from the roofs of the tunnels. These are white and contain much water. A qualitative analysis by Mr. F. A. Hall showed them to be a natural alum.

A most interesting altered form of the andesite is exposed in the lower Victoria tunnel for a distance of 150 feet, not far below the contact between limestone and andesite. It is a yellowish rock, secondarily enriched with silica, which breaks with a conchoidal fracture. The rectangular crystals of feldspar a quarter of an inch or less in diameter have been replaced by opaline silica. They show a zonal structure where a milk-white core is surrounded by a glassy colorless border. Abundant irregular pieces of native copper have been included by the silica. Minute crystals of pyrite may readily be observed with a lens.

Under the microscope the normal andesite is found to contain large crystals of a basic plagioclase (labradorite) which show a zonal structure and are twined on the Carlsbad and albite laws. They yield small amounts of calcite on weathering. Biotite is present in long chestnut brown, rectangular patches, hornblende in dark green crystals showing blunted ends is hardly less abundant. The ground-mass is a fine-grained aggregate of feldspar crystals, among which occasional apatite needles are met.

The relations between andesite and limestone have a direct bearing upon the origin of the ore deposits. The question regarding the relative ages of the two rocks is still open with all the evidence obtainable at hand. The writer believes, however, that the andesite is without doubt younger than the limestone. In opposition to this view is the fact that in no instance whatever does the limestone appear metamorphosed where it lies against the andesite. More than half of all the mine workings are along the contact between the two rocks so that the area exposed to observation is relatively large. No inclusions of the limestone could be found. Again no good instance of a dike was observed. A single tunnel five feet by seven may run through limestone-andesite contacts five times in going fifty yards, with the lines of contact passing from hanging to foot wall yet it cannot be held as certain that the andesite has sent dykes into the limestone. In the mine workings as a rule the hanging wall is limestone, the foot



wall andesite. The contact between the two is wavy and quite irregular. Consequently the levels often pass through successive sags of the limestone on the andesite. No dikes were observed at the surface nor yet running out from the igneous mass into the limestone. The underground workings, however, give two instances where the andesite has sent out pointed stringers less than a foot wide into the limestone. With the exception of these finger-like bodies the evidence as to the age of the andesite is negative. Its character as a medium-grained porphyritic rock coming up to the contact without change of texture is not unusual for laccolithic bodies. The chief reason for believing that the andesite is younger than the limestone is in the evident connection be-

tween the ore deposition and the igneous rock. No prospects have offered even slight encouragement at a distance from the andesite mass. All the mines in the limestone are within a few feet of the andesite, and are connected with it by feeders. The mineralized zone, as before stated, immediately surrounding the andesite is of small extent. The lowest workings in all the mines touch andesite. A diamond drill in the Victoria tunnel has gone down through it vertically for a distance of 450 feet without encountering any other rock. No proof is at hand to show that the andesite has the form of a laccolith. It seems rather to be an irregular knob with an upper surface as shown in the section, page 65. The periphery of the mass has not been reached in any direction in the mine workings, and the writer does not believe that exploration with the diamond drill will show the presence of anything but barren andesite in depth.

With scarcely an exception the ore bodies lie along the limestone-andesite contact, or in the limestone at a short distance from the igneous rock. Small stringers and veins, but no large deposits, are found in the andesite. Over 70 great chambers of ore have been found, ranging in size from 1,000 to 100,000 cubic yards. Where they are entirely surrounded by the limestone they often show a tendency to follow the stratification planes. The ore bodies are usually connected one with another. They commonly send out stringers into the wall rock. They appear as irregular lenses and kidney-shaped masses, filled entirely with oxidized ores. Secondary veins of sulphides are rare. It should be noted that although the ore chambers are often connected one with another, there are many exceptions to this rule. The ores do not run down in depth as a continuous shoot. The ground water has not been reached in any of the deep workings, nor do these show anywhere that they are near it. It is not to be expected therefore that a lower zone of sulphides, if it exists, will ever be reached. The pay ores are all above the andesite mass, and there is no appreciable difference between the highest and the lowest ore bodies until it is reached.

At the San Pedro mines gold occurs native. Crystals have often been obtained but no compounds of the metal are known. Silver is occasionally found native, and the chloride cerargyrite is not infrequently met with in the workings. Ninety-five per cent. of the metal, however, comes with the lead. The ore of lead at San

Pedro is the carbonate, cerussite. Galena is scarcely ever found, and then in secondary veins rarely two inches in width. Copper is almost a curiosity. The minerals which contain it are malachite and chrysocolla. Hard blue hematite with the softer red oxide is the most common mineral present in the district. It carries the native gold though often found with no trace of it. Small amounts of the iron are hydrated and show as limonite. Residual chert is constantly found through the ore bodies and much calcite, with

Part of the caved territory, Cata Santos and San Nicolas.

the hematite, as gangue. Arsenic is present in very small amounts with traces of antimony. Zinc is not known.

Any statement regarding the manner of formation of the San Pedro ore bodies, must recognize the prominent part played by the igneous phenomena represented in the basal andesite, and should satisfactorily account for the size and distribution of the ore chambers in the limestone. From assays of the rhyolite it is not believed that this rock exercised any influence on the ore deposition. The limestone is likewise barren. Assays of the andesite, on the other hand, constantly indicate the presence of gold and silver in the proportions of one to ten, *i. e.*, with two

grams of gold to the ton, 20 grams of silver. Mr. Laird has observed that this ratio between the precious metals has held as the average in gold and silver values for 20,000 tons of ore shipped from the mine under his management. He is of the opinion, therefore, that the gold and silver values were derived from the andesite, and there is no reason to question the soundness of this view. The writer believes that the enormous bodies of iron were deposited in the limestone before the coming of the solutions

Guadalupe terminal of tramway and general view of hills.

which carried the gold and silver. The limestone, although at present much folded, and dipping at high angles, is evenly bedded and massive. It has plainly been a prey to the solvent action of surface waters. The forms of the ore bodies are such as a system of underground drainage in a limestone region would yield. At a distance of 30 miles from San Pedro, where the limestone strata are undisturbed, a very extensive underground drainage with sinkholes and caves is found. It is probable that at San Pedro large bodies of iron oxide were precipitated in underground chambers from passing ferruginous solutions. The residual soil which has resulted from long-continued weathering of the overlying rocks is

everywhere deeply charged with iron. The deposition of a portion of the lead which now appears as the carbonate, with silver values, was effected side by side with the laying down of the iron, from circulating waters which had probably taken the metals from overlying limestone strata. The amount of lead present is perhaps one seventh of the iron. No facts could be observed which proved that the lead had been deposited originally as the sulphide. After the deposition of the baser metals, with some silver, and the folding of the strata which contained them, the coming of the andesite brought with it heated alkaline solutions bearing the gold, with silver, which was then laid down throughout the ore bodies along the joints and small fissures produced by the folding.

THE GEOLOGY OF THE CERRILLOS HILLS, NEW MEXICO.

By DOUGLAS WILSON JOHNSON.

PART III. PETROGRAPHY.

The igneous rocks of the Cerrillos Hills have long attracted attention, more especially because of their association with the famous turquoise deposits and the anthracite coal of the region. The following pages represent an attempt to secure some evidence concerning the origin and method of occurrence of the turquoise, and to work out the relations of the associated rocks. The investigation of this problem was prosecuted with the aid of a grant from the Herrman Fund of the Council of the Scientific Alliance of New York.

With two minor exceptions, the igneous rocks of the Cerrillos region are of post-Cretaceous age. The exceptions consist of a few very small exposures of volcanic breccia and mica andesite, the former interstratified with Laramie (?) beds, and the latter with beds of the Colorado group.

The entire mass of the Cerrillos Hills proper is composed of rocks belonging to the augite andesite series, while a portion of the lower country to the east is formed by hornblende andesite. The intruded sheets or sills of the Madrid area south of the hills consist of a rock belonging to the hornblende andesite series, but

showing trachytic affinities. Rocks of the olivine basalt series occur, forming Mount Calvary, and the low crater and surface flow northwest of the hills. Dykes of the augite andesite and basalt series are abundant. We have then, in the Cerrillos region, the following series of eruptives, given in the order of their relative ages, the oldest first:

1. Mica andesite series.
2. Eruptive breccias.
3. Hornblende andesite series.
4. Augite andesite series.
5. Olivine basalt series.

As these rocks occur in the form of interstratified beds, intruded sheets or sills, laccoliths, surface flows and dykes, the same rock occurring in several of these forms, a considerable variety of texture is developed. It is desirable, at the start, to define the rock names as used in this report, although the usage is not new, the classification being based on both textural and mineralogical variations.

An andesite is an igneous rock of porphyritic or felsitic texture, whose feldspathic component is dominant and is chiefly plagioclase, and which contains one or more of the following: biotite, hornblende, augite. According to which of the latter minerals is most prominent, we have mica andesite, hornblende andesite or augite andesite. If two of these minerals are present in a very notable degree, both are represented in the rock name, the name of the dominant mineral appearing first; as in hornblende-augite andesite.

By trachy-andesite is meant an igneous rock of porphyritic or felsitic texture whose feldspathic component dominates, and consists of more or less nearly equal amounts of orthoclase and plagioclase, and which has one or more of the following: biotite, hornblende and augite. It is thus intermediate between trachytes and andesites.

By gabbro-porphyry is meant a rock consisting of dominant plagioclase, and a monoclinic pyroxene, and which closely approaches a granitoid texture, but in which the pyroxene has its own crystal boundaries more or less perfectly developed. Texturally, the rock is intermediate between a true porphyritic augite andesite and its thoroughly granitoid representative, gabbro.

By augite monzonite-porphyry is meant a rock whose feldspathic

component is dominant and consists of plagioclase and orthoclase in more or less nearly equal amounts, whose chief ferro-magnesian mineral is augite, and which closely approaches a granitoid texture, but in which the augite has its own crystal boundaries more or less perfectly developed. Mineralogically, the rock is intermediate between gabbro and augite syenite; and since the name monzonite is used to designate rocks intermediate between diorite and hornblende syenite, it seems desirable to apply the name augite monzonite to a rock which differs from the typical monzonite only in the presence of augite in place of the hornblende. Texturally, the rock is intermediate between a truly porphyritic trachy-andesite and its thoroughly granitoid representative, the monzonites.

Olivine basalt and limburgite are used in the usual well-established senses, the former to designate an igneous rock of porphyritic or felsitic texture with dominant ferromagnesian components, containing olivine, with its chief feldspar plagioclase; the latter to denote a similar rock in which the feldspar is absent.

By a rock "series," as the term is here employed, is meant the typical rock and those variations which appear to be merely mineralogical or textural variations of the same mass. Thus the augite andesite series includes the typical augite andesite, the gabbro porphyry, which is a textural variation of the same rock, and the augite monzonite-porphyry, which is both a mineralogical and textural variation of that same rock.

Although in the discussion of general geologic features, as set forth in Part I. of this report, the broader names of the several rock series alone were most frequently employed, it is desirable in connection with the detailed petrographical description to recognize the following subdivisions, which will be taken up in order:

1. Mica andesite series.
   (*a*) Mica andesite.
2. Eruptive breccias.
3. Hornblende andesite series.
   (*a*) Hornblende andesite.
   (*b*) Hornblende-augite andesite.
   (*c*) Hornblende-augite trachy-andesite.
4. Augite andesite series.
   (*a*) Augite andesite.
   (*b*) Gabbro-porphyry.

(*c*) Augite monzonite-porphyry.

5. Olivine basalt series.

(*a*) Olivine basalt.

(*b*) Limburgite.

The discussion of the turquoise matrix is given in connection with the description of the augite andesite series, while the consideration of the turquoise itself is given in a final section.

Literature.

In the literature of the region we find many references to the rocks of the Cerrillos Hills proper, as well as to the rocks composing the outlying hills. As a rule the determinations were made on megascopic characters only, and for the practical purposes of field records alone. Only the later observers made microscopic or chemical examinations, with a view to determining the rocks more closely.

Jules Marcou (1853) reports "trachyte et roche pyroxènique, trap," and says "Quelquefois ce trap est basaltiforme."* Professor W. P. Blake (1857) studied the turquoise deposits at Mt. Chalchihuitl, and described the rock as "a granular porphyry, yellowish, gray and white, in color; porous and earthy in texture. It decomposes rapidly by weathering, and very much resembles a sandstone."† This is the decomposed phase of the augite andesite, hereafter to be described. Dr. Newberry (1859) described the rocks composing the Cerrillos Hills as "wholly eruptive in character, mainly trap and trachyte," and the rock of Mt. Chalchihuitl as "a yellow porous trachytic porphyry."‡

Dr. F. V. Hayden (1869) does not refer to the nature of the eruptives of the Cerrillos district, but regards the Hills as composed of a dyke or a series of dykes.§ Dr. Oscar Loew (1874) regarded the Cerrillos Hills as composed of basalt and trachyte, and in his report gives an analysis of the turquoise.‖ Professor J. J. Stevenson (1879) described the Cerrillos Hills as relics of huge trachyte dykes, and also reported the occurrence of basalt in the region.¶

* Mississippi Railroad Reports, Vol. III., Pt. IV., p. 141.

† *Am. Jour. Sci.*, March, 1858, p. 229.

‡ Rep. of Expl. Exped. from Santa Fé, N. Mex., to Junction of Grand and Green Rivers, Macomb; Geol. Rep. by Newberry, p. 41.

§ Prelim. Field Rep. U. S. Geol. Surv. of Colorado and New Mexico, p. 67.

‖ Rep. Chief of Engineers, 1875, Pt. II., p. 1027, 1028.

¶ U. S. Geog. Surv. west of 100th Mer., Vol. III. Supplement, pp. 329, 330, etc.

Professor B. Silliman (1880) studied the turquoise deposits, and wrote: "These rocks are all eruptive rocks of the family of the augite trachytes."* In another place he refers to the "hard and tough hornblende andesite, or propylite, which forms the Cerro d' Oro and other Cerrillos Hills."† Professor Silliman's determinations were based on microscopic examinations. Professor J. F. Kemp (1896) made a microscopic examination of the rocks in the Madrid area, a small suite of which were submitted by Prof. J. J. Stevenson, and published the results of his examination in connection with Professor Stevenson's report on "The Cerrillos Coal Field."‡ Professor Kemp regarded these rocks as trachytes with close affinities for andesites.

Dr. C. L. Herrick (1898) noted one of the interstrata flows near the top of the Galisteo Monocline as being composed of "a characteristic leucite phonolite."§ He regarded the southern part of the Cerrillos group as being composed of this phonolite, and the northern part of granite, and described the basalt flow northwest of the hills. In a more recent paper‖ Dr. Herrick speaks of the Cerrillos Hills as having a small core of andesite surrounded by later material, the southern part of the group being composed of aegirine syenite.

The results of my own studies in the region are given below. Over two hundred typical rock specimens were secured, representing the phases of the eruptives occurring in all parts of the area. A study of over a hundred thin sections served to establish the characteristic types, as well as their areal limits with a fair degree of accuracy.

1. Mica Andesite Series.

(*a*) *Mica Andesite.*

Several interstata sheets in the district are composed of a very peculiar rock which is so greatly altered as to make its true characters difficult to ascertain. A couple of miles northwest of Waldo is exposed in Cretaceous shales, one of these sheets about two feet in thickness. The rock is dull grayish in color, evidently greatly

* *Am. Jour. Sci.*, July, 1881, p. 68.

† *Ibid.*, p. 70.

‡ *Trans. N. Y. Acad. Sci.*, 1896, p. 122.

§ *Bull. Univ. New Mex.*, Vol. I., pp. 109, 110.

‖ Report of Governor of New Mexico for 1900, p. 259.

decomposed, and is full of elongated cavities filled with calcite, some of which are nearly as large as a man's little finger. Under the microscope abundant rods of plagioclase and shreds of biotite can be seen, but little else can be made out, save the calcite. As in similar rocks larger pieces of biotite are also visible, I have regarded this specimen of one of the mica andesites. It seems most probable that the rock represents a surface flow in Cretaceous (Colorado) times, which was filled with steam cavities, and that the slow movement of the nearly solidified mass at this point produced the elongation of the cavities which were later filled with calcite derived from the surrounding shales. That this flow may have spread out over the floor of the Cretaceous sea is suggested by the occurrence of the fossiliferous shales immediately above and below the flow.

Near the top of the Galisteo Monocline, 100 feet below the intruded sheet of augite andesite elsewhere referred to, a rock somewhat similar to the foregoing occurs as an interstrata sheet about a foot thick. This rock is darker than the former, but filled with small rounded masses of light substance, giving it a peculiar mottled appearance. Under the microscope the rock is seen to be a mass of spherulites of limonite-stained feldspars, with long, fine shreds of biotite (?) and occasional larger pieces of the same scattered throughout. Both the dark base of the rock and the light rounded masses are of the same spherulitic aggregates. Calcite occurs filling cavities. It seems not improbable that this rock is the same as the preceding, and that the calcite-filled cavities represent original amygdaloidal cavities. Fossils of Colorado age are found just above this sheet.

West of Cerrillos about a mile, in the shales dipping sharply away from the laccolith, is a small interstrata sheet of rock very similar to the preceding, except that it is much lighter and the rounded masses in it are less numerous. The microscope shows the remains of a few altered phenocrysts of plagioclase, while the great mass of the rock including the large light-colored spherules is made up entirely of beautiful little spherulitic aggregates (Plate Q, Fig. 1). Decomposition is too great to make out the minerals of the spherulites. Plagioclase is probably the main component, although a little green chlorite seems associated. Calcite is abundant.

If these three exposures are parts of one surface flow, as seems not unlikely, they represent the oldest rock in the region. If horn-

FIG 1 —SPHERULITIC MICA ANDESITE (?). (Between crossed nicols.)

FIG. 2.—HORNBLENDE-AUGITE ANDESITE. (Between crossed nicols.)

blende and augite occurred in this rock before its profound alteration, as is not impossible, or if they occurred in associated flows, we have a suggestion as to the age of the andesite fragments in the volcanic breccias found in the later Cretaceous beds of the Galisteo Group.

2. Eruptive Breccias.

East of the Cerrillos district, where the red sandstones of the Galisteo group have resumed the normal dip of several degrees to the east, occur large beds of eruptive breccia interstratified with the sandstones. The beds aggregate over a hundred feet in thickness, and are divided by occasional thin lenses of red sandstone. They represent the accumulations resulting from explosive outbursts of some volcano situated near a shore-line of the late Cretaceous sea, whose successive periods of activity were only far enough apart to permit the formation of thin lenses of sandstone between the eruptions. That the ejectamenta fell in shallow water near the shore is indicated by the fact that the material is beautifully sorted and stratified, and lies upon sandstones in which horizontal fragments of tree trunks are found. None of this silicified wood was found in the breccia itself, but occurred at the top of the sandstone bed immediately under the breccia. The more extensive deposits of the "petrified forest" occur a short distance west, at a lower horizon.

The stratified character of these beds is well shown in Plate J, where the hammer is held at the contact with the underlying sandstones. The material varies in size from fine sand to boulders two and three feet in diameter. In some places consolidation has been developed to a fairly marked degree, and the breccia is used as ballast quite extensively by the Atchison, Topeka and Santa Fé railroad. It may be seen at various points along the road for many miles in either direction. The most accessible and extensive deposits occur near Ortiz, a station several miles farther east.

In the Cerrillos district are a number of exposures of the Galisteo group in the midst of the eruptive area, either turned up by one of the smaller laccoliths or caught up in the midst of the lava itself. In one instance the portion of this series containing the breccia was evidently thus caught up, for a little over a mile east of Grand Central Mountain is a limited area of the breccia, exposed in one of the small arroyos. The stratified character is well developed

and shows a dip of several degrees to the west. At the western base of Mount Calvary, on the northern boundary of the district, is another small exposure of the breccia, dipping very gently northeast.

Under the microscope the breccia is seen to be composed of angular fragments of hornblende andesite, augite andesite, quartz grains, orthoclase, plagioclase and hornblende crystals, in a cement deeply stained with limonite. Occasional microcline suggests fragments from the old crystallines, while some of the orthoclase grains show beautiful zonal structure. Resorption of the hornblende in the andesite fragments was noted in a specimen from the locality east of Grand Central Mountain. Calcite as a decomposition product is abundant. No glass was observed, and it is evident that the fragments were torn from the solid rocks in depth and blown out in this condition. The resorption referred to must have taken place at a time previous to the eruption and wholly independent of it.

The andesite fragments are of a lighter color than the finer material found together with the deep red cement and are readily recognized. It is worthy of note that the two principal eruptives of the Cerrillos district are here represented, rocks of both the hornblende and augite andesite series. A careful comparison of these fragments with the types of the Cerrillos massive eruptions is difficult, because of the fragmentary and somewhat altered condition of the former. In general, however, the andesite fragments of the breccia correspond quite closely with some of the more decidedly porphyritic phases of the later intrusives. There is a pronounced and finely crystalline groundmass as a rule, while the feldspar phenocrysts, of both orthoclase and plagioclase, are better developed in some of the fragments than in the later rocks. In some cases these fragments are of hornblende vulsinite, hornblende being the only ferromagnesian mineral apparent, while orthoclase and plagioclase phenocrysts are present in nearly equal amounts.

That these andesite fragments are from rocks older than the Cerrillos andesite series there can be no doubt. The breccias containing them were formed in late Cretaceous times, during the deposition of the beds of the Galisteo Group. These beds and the interstratified breccias were upturned by the andesite intrusions forming the Cerrillos Hills. The evidence points to an andesitic magma which was tapped at successive geological times, yielding lavas of much the same general character.

3. Hornblende Andesite Series.

(a) *Hornblende Andesite.*

The true hornblende andesite is confined to the eastern side of the Cerrillos Hills, constituting the country rock of the area drained by the tributaries on the northwest side of San Marcos Arroyo. Nearer Cerrillos the hornblende andesite is found on the southeast side of the arroyo, where it forms one of the smaller outlying laccoliths. The approximate areal limits are shown on the geological map.

As shown in the discussion of the general geology, the hornblende andesite is probably older than the rocks of the augite andesite series which compose the Cerrillos Hills proper, and occurs in the form of several laccoliths more or less intimately associated with each other. The rock is almost always somewhat decomposed, presenting a marked contrast with the usually fresh material of the later series.

In typical cases the rock is markedly porphyritic, phenocrysts of hornblende and plagioclase occurring in a finely crystalline groundmass. Magnetite as a rule is not abundant, and apatite is universally present in small amounts. Biotite rarely occurs in small shreds, usually more or less decomposed. Chlorite, and infrequent epidote, appear as alteration products. Calcite is quite common. Orthoclase may be present, but is usually very subordinate. Garnet was found in a specimen from half a mile west of the Reservoir in San Marcos Arroyo, while a little farther south a specimen showed occasional ilmenite with its characteristic decomposition product, developed along more or less definite rhombohedral directions. Titanite is rare.

The phenocrysts of plagioclase are usually much decomposed, so that the twinning is often greatly obscured. They may become quite large, giving the typical "bird's eye porphyry" appearance in the hand sample. Optical determinations show that the plagioclase is quite uniformly the variety oligoclase. Southwest of the reservoir in San Marcos Arroyo the andesite shows unusually fresh zonal feldspars, mostly plagioclase. In some cases calcite has replaced the more basic centers of these crystals. The hornblende is rarely well preserved, but occasionally shows fairly good crystals of the green variety. As a rule it is wholly gone over to chlorite, the outlines of the original crystal, however, being quite

well preserved. Occasionally beautiful examples of the "Berlin blue" polarization effects are to be seen in this chlorite.

As a variation of the typical hornblende andesite we have a specimen from northwest of the reservoir which is composed almost entirely of plagioclase. Magnetite is very rare, and only a few small remnants of the hornblende are to be seen.

(*b*) *Hornblende-Augite Andesite.*

This phase (Plate Q, Fig. 2) of the andesite series differs from the foregoing in having a notable amount of augite among the phenocrysts. The augite is usually inferior to the hornblende in quantity and occurs as rather small, pale green, automorphic crystals.

The plagioclase is of the variety oligoclase, and as a rule occurs in smaller crystals than is usual in the preceding rock. The hornblende phenocrysts are almost wholly resorbed, a mass of small magnetite grains indicating the original form of the crystal. The augite, on the other hand, remains quite fresh in cases. Beautiful spherulitic chlorite is occasionally found, while calcite is not uncommon. Magnetite occurs often surrounded by reddish limonite. Apatite is rare, and a little orthoclase may be present.

This rock occurs half a mile northeast of Poverty Hollow, where it is surrounded by the typical hornblende andesite, and appears to be merely a phase of it. That the conditions were different in this portion of the magma is shown by two facts: Augite formed and remained; hornblende formed, but the conditions were such that after eruption it suffered resorption, whereas in the surrounding rock the hornblende remained, and was only changed at a later time, by secondary alteration, into chlorite.

A variation from the above type occurs at the western end of Grand Central Mountain, right in the midst of the augite andesite. In this case the hornblende has not been resorbed, but decomposed, forming an indistinct aggregate which seems to be chlorite. The apatites are unusually large, being short and thick. This may be an unusual phase of the surrounding augite andesite, or more likely an inclusion of the older hornblende andesite series. Near here is a large inclusion of Cretaceous shales.

Still another variation occurs in one of the interstrata sheets in the Madrid area. A section of the fairly fresh rock, brought up as a drill core, showed an unusually large proportion of the augite, while the hornblende was of a beautiful pale greenish-brown

variety. The columnar habit of both the augite and hornblende is well developed, and long lath-shaped sections are frequently seen under the microscope. Magnetite occurs, and apatite is rather abundant. Calcite and pyrite are present in small amounts.

(*c*) *Hornblende-Augite Trachy-Andesite.*

This type of rock is characteristic of the Madrid area, where it occurs as intruded sheets or sills. It differs from the more widespread andesites of the Cerrillos district in its large percentage of orthoclase feldspar, thus making it intermediate between the andesites and trachytes. The feldspars occur as large phenocrysts and also in the finely crystalline ground mass, the plagioclase phenocrysts being of the variety oligoclase. The pale greenish-brown hornblende is much more abundant than the augite, which is of the light green variety. Both of the ferromagnesian minerals also occur as small shreds. The magnetite is only moderate in amount, and apatite occurs as usual; titanite is rare. A few grains of quartz are also present, but are very rare. A little calcite is seldom seen.

A specimen from the eastern base of the Ortiz Mountains, in which group the sills of the Madrid area originate, shows the hornblende occurring about the outer edges of the augite, as a parallel growth. In this specimen there is considerable magnetite, and the apatites are unusually large and abundant.

4. Augite Andesite Series.

(*a*) *Augite Andesite.*

This is the most abundant rock of the Cerrillos district, and forms several of the larger peaks of the Cerrillos Hills proper, as well as several of the outlying smaller hills. It is also the most common rock in the dykes and sills surrounding the main laccolithic uplift.

Mineralogically the rock does not differ essentially from a true augite andesite. The typical variety is markedly porphyritic. Automorphic phenocrysts of pale green augite are abundant, occasionally showing the usual twinning phenomena. Not uncommonly inclusions of rutile needles forming "sagenite" webs are seen in the fresh augite. Of the usual inclusions magnetite and apatite are rarely quite abundant. In a specimen from east of the reservoir in San Marcos Arroyo, coming from a very small ex-

posure of brecciated material, the augites are beautifully zonal, and occasionally show wavy extinction. The augite may also occur as a second generation in the ground mass, in the form of tiny rod-shaped crystals or shreds. In a specimen from the northwest base of Mt. McKensie the little rod-shaped crystals are abnormally developed, giving the section a very peculiar appearance. In the fresh rock forming the central portion of Turquoise Hill the augite phenocrysts are notably rounded by corrosion. In many cases the rock is more or less decomposed, and the augite is altered to epidote and calcite — more rarely to chlorite.

The feldspars occur in good automorphic or more fragmentary phenocrysts of plagioclase and rarely of orthoclase. The plagioclases range from andesine through the less basic of the labradorites. The usual twinning phenomena are observed, that according to the Baveno law being rare. Good zonal structure is occasionally seen. As the decomposition of the rock progresses, it is noted that the decay of the feldspars results in the obliteration of visible twinning phenomena before the crystal outlines are wholly obscured. All stages of the process are to be noted, and individuals which at first sight appeared to be a somewhat altered untwinned feldspar, with fair crystal boundaries, on more careful examination showed the faintest traces of albite twinning. It is possible that this may explain the statement by some that the rock in which the turquoise occurs contains only orthoclase feldspar, since the more unaltered portions of the same rock, only a few feet distant, contain few feldspars that are not undoubted plagioclase. The plagioclases also occur in the groundmass as small lath-shaped crystals and as irregular shreds. Frequently the groundmass is almost wholly composed of this feldspar, while in cases kaolinization is so extensive as to suggest its great abundance, although individual crystals are not recognizable.

Biotite is frequently present in small amounts, generally altered. It is sometimes most abundant about magnetite grains. Where fresh and in large fragments, it is of the brown, strongly pleochroic variety, changing from a pale yellowish-brown to a deep chestnut color. The magnetite may be quite rich, or may almost fail entirely. Apatite is not abundant as a rule, occasionally occurring as large, thick crystals. Zircon was noted in only one instance. In the more decomposed phases calcite and limonite are common. Pyrite is rare. Quartz was occasionally noticed, especially in the

FIG. 1.—GABBRO-PORPHYRY FROM MT. MCKENSIE. (Between crossed nicols.)

FIG. 2.—AUGITE MONZONITE-PORPHYRY FROM SANTA ROSA MOUNTAIN. (Between crossed nicols.)

central portions of the laccolithic masses. In one of the large dykes, northwest of Waldo, little spherulitic aggregates of tourmaline were seen.

A peculiar phase of the andesite occurs as an interstrata sheet at the top of the Galisteo Monocline, west of the hills. The rock does not differ essentially from a true andesite, but contains a notable amount of an hexagonal mineral sq badly decomposed as to make its identity a little uncertain. It seems most likely that it was nephelite. Dr. Herrick regarded the mineral as leucite, and on it probably based his reports of leucite phonolite from the region. In the same slide is a single section of a dark brown mineral which appears to be allanite. The augites of this rock are notably pleochroic.

In many of the radiating dykes of the region the porphyritic texture of the typical andesite is encountered, while in other cases the texture is noticeably different. Thus in some of the dykes east of the hills, the prominent dyke in Ortiz Arroyo south of Cerrillos, and the big Madrid dyke in Coal Gulch, we find few if any large phenocrysts. The rocks are fine-grained, as a rule, but almost entirely holocrystalline. Small rod-like crystals or shreds of augite are very abundant, together with rode-like and irregular plagioclases. Biotite is present in notable amounts, while considerable magnetite and very little apatite are seen. In one of the dykes east of the hills a little isotropic interstitial mineral was noted, which is probaly analcite. In the case of the Madrid dyke the augites are unusually abundant, and are of the violet-tinted variety more common in the basalts. These rocks are very similar to the camptonites of Rosenbusch.

(*b*) *Gabbro-Porphyry.*

On a textural basis we may establish a very important phase of the augite andesite, which is characteristic of the central portions of the greater laccolithic masses. The rock shows abundant automorphic crystals of augite, while the feldspars approach the granitic habit in their development, being more or less completely prevented by neighboring crystals from attaining perfect crystal boundaries. To this phase we might appropriately apply the name "gabbro-porphyry." It differs from the typical andesite in the absence of a distinct ground mass, and the approach to a granitic texture. The rock of Mt. McKensie (Plate R, Fig. 1) is a

good example of this phase, while that of Grand Central Mountain is similar, but contains a notable amount of orthoclase. Biotite is fairly abundant in both of these rocks.

The gabbro-porphyry in the best preserved rock of the andesite series, and affords the best material for analysis. It is not probable that it differs materially in chemical composition from the porphyritic phases of the andesite just described. The chemical analysis, prepared by Dr. George Steiger, of the United States Geological Survey, is given under No. 1 in the table below.

A rock of very similar chemical composition is reported from the pass south of Mount Sneffels, Telluride quadrangle, Colorado.* It is called a gabbro-porphyry, and judging from the description differs mineralogically from our rock in the presence of hypersthene, the more pronounced groundmass and lack of large automorphic augites. The analysis of a plagioclase basalt from Saddle Mountain, Colorado,† is closely similar, being a little lower in alumina. A limburgite from Stein in Styria, Austria,‡ is a little lower in silicia and higher in magnesia. These relations are more clearly shown in the following:

TABLE OF ANALYSES.

	1.	2.	3.	4.
SiO_2	48.21	47.32	48.76	46.76
Al_2O_3	17.96	16.71	15.89	17.93
Fe_2O_3	5.18	6.92	6.04	5.33
FeO	4.47	5.94	4.56	5.62
MgO	4.11	5.69	5.98	7.31
CaO	9.72	8.51	8.15	8.24
Na_2O	3.68	2.70	3.43	3.53
K_2O	2.99	2.02	2.93	2.20
H_2O+	1.41	1.04	1.48	} 1.83
H_2O-	.21	.24	.40	
CO_2	none.	none.	.....	1.33
TiO_2	.84	1.50	1.65	trace.
ZrO_2	none.	.....	none.	.....
P_2O_5	.58	.96	.60	.....
SO_3	none.	.19	.....	.....
Cl	.....	trace.	.....	.....
MnO	.31	.08	.13	trace.
BaO	.07	.07	.17	.....
SrO	trace.	.06	.06	.....
Li_2O	.....	trace.	none.	.....
Total.	99.74	99.95	100.23	100.08

* Bull. U. S. G. S. No. 168, p. 163, 1900.

† *Jour. Geol.*, Vol. V., p. 689, 1897.

‡ *Tsch. Min. u. Pet. Mit.*, Band 17, S 534, 1898.

No. 1. Gabbro-porphyry from Mt. McKensie, Cerrillos Hills, New Mexico. Dr. George Steiger, analyst.

No. 2. Gabbro-porphyry from pass south of Mt. Sneffels, Telluride quadrangle, Colorado. H. N. Stokes, analyst.

No. 3. Plagioclase basalt from Saddle Mountain, Colorado. W. F. Hillebrand, analyst.

No. 4. Limburgite from Stein, Styria, in Austria. Herr Dr. Richard R. v. Zeynek, analyst.

The classification of the Cerrillos rock according to the scheme recently proposed by Cross, Iddings, Pirsson and Washington * proves of interest. After calculating the molecular proportions of the chemical components of the rock from the complete analysis, and effecting the distribution of these components as mineral molecules, the percentage weights of the minerals were obtained and the *norm* established as shown below:

Formula.	Mol. Wt.	Norm.				
$K_2O.Al_2O_3.6SiO_2$	32×556	= Orthoclase = 17.79	F	60.00	Sal.	66.82
$Na_2O.Al_2O_3.6SiO_2$	36×524	= Albite = 18.86				
$CaO.Al_2O_3.2SiO_2$	84×278	= Anorthite = 23.35				
$Na_2O.Al_2O_3.2SiO_2$	24×284	= Nephelite = 6.82	L	6.82		
$CaO.SiO_2$	77×116	= Diopside = 17.11	P	17.11	Fem.	31.32
$MgO.SiO_2$	62×100					
$FeO.SiO_2$	15×132					
$2MgO.SiO_2$	41×70	= Olivine = 3.79	O	3.79		
$2FeO.SiO_2$	9×102					
$FeO.Fe_2O_3$	33×232	= Magnetite = 7.66	M	9.18		
$FeO.TiO_2$	10×152	= Ilmenite = 1.52				
$3CaO.P_2O_5$	4×310	= Apatite = 1.24	A	1.24		
		H_2O = 1.62				
		99.76				

Class II.	Order 5.	Rang 3.
$\frac{Sal}{Fem} = \frac{66.82}{31.32} < 1\frac{1}{2} > 1\frac{1}{3}$	$\frac{L}{F} = \frac{6.82}{60.00} < \frac{1}{4}$	$\frac{K_2O' + Na_2O'}{CaO'} = \frac{92}{84} < 1\frac{1}{3} > 1\frac{1}{3}$
Dosalane.	*Germanare.*	*Andase.*

Subrang 4.	Grad 1.	Subgrad 1.
$\frac{K_2O'}{Na_2O'} = \frac{32}{60} < \frac{1}{2} > \frac{1}{4}$	$\frac{P + O}{M} = \frac{20.90}{9.18} > \frac{1}{2}$	$\frac{(Mg.Fe)O + CaO''}{K_2O'' + Na_2O''} = \frac{251}{0} > \frac{1}{2}$
Andose.	*Andate.*	*Andote.*

From this it appears that the Cerrillos rock, which has been classified on a purely mineralogical basis as a gabbro-porphyry phase of true andesite, on the basis of the proposed chemico-mineralogical classification falls under *Andose.* Andose is a subrang of Rang

* "Quantitative Classification of Igneous Rocks," Chicago, 1903.

3, Andase, the type rock of which rang is the andesite of the Andes mountains. As shown by the calculation, the andose is dosalic (having the silico-aluminous non-ferromagnesian group of standard minerals dominant); is perfelic (extremely rich in normative feldspar); is alkalicalcic (having the alkalies and calcium in nearly equal amounts in the salic minerals); is dosodic (having soda dominant over potash); is prepolic (having the ferromagnesian silicates dominant over the ferromagnesian non-silicates); and premirlic (having the magnesium, iron and lime of the ferromagnesian minerals dominant over the alkalies of these same minerals). Accordingly the rock belongs in Class II., Dosalane; Order 5, Germanare; Rang 3, Andase; Subrang 4, Andose; Grad 1, for which I suggest the name Andate; and Subgrad 1, for which I suggest the corresponding name Andote. According to Dr. Washington Grad 1 and Subgrad 1 are the most typical and common for the Andoses, a very large group. For this reason it seems best that they should be known respectively as andate and andote. The type of this magma represented by the Cerrillos rock might be known as the "cerrillal type," and the habit as the "cerrilloid habit," following the outline suggested by the authors of the new scheme.

The chemical analyses of Nos. 2, 3 and 4, in the preceding table of analyses, were suggested by Dr. Washington as showing the composition of other closely related rocks, all of them belonging in andose, and having low silica. It is thus seen that a gabbro-porphyry, a plagioclase-basalt and a limburgite are grouped together under the same subrang, being chemically much alike although differing widely mineralogically.

The Cerrillos rock furnishes a good example of one of the objections urged against the proposed classification, viz.: the difference between the standard mineral composition, or norm, and the actual mineral composition or mode, as determined under the microscope. The standard mineral composition gives for the rock about eighteen per cent. of orthoclase, seven per cent. of nephelite, seventeen per cent. of diopside, and four per cent. of olivine. Actually (modally) the rock contains little or no orthoclase, no nephelite, diopside or olivine, but a goodly percentage of augite and biotite not shown by the norm. On the other hand, a notable amount of orthoclase is present in the rock of some of the neighboring peaks, while a decomposition product from what may have been nephelite is found in a sill several miles west of the Hills.

According to a note from Dr. Washington "The normative orthoclase and olivine are present modally in the biotite. As the pyroxene contains undoubtedly a considerable percentage of the pure "augite" molecule (Mg, Fe)O.Fe_2O_3.SiO_2, this mineral will take up most, if not all, of the normative magnetite (and ilmenite). The normative diopside will also enter into this mineral. This transfer of Fe_2O_3 from magnetite to augite will bind an amount of SiO_2 equivalent to the Fe_2O_3 so transferred, leaving less silica available for combination with the Na_2O, and thus increasing the potential amount of nephelite. As, however, we have shown that in the biotite of such rocks the ratio of (Mg, Fe)O to the K_2O is about 5 : 1, it is evident that, to satisfy these conditions, some of the (Mg, Fe)O of the hypersthenic molecules of the normative diopside must exist modally as olivine molecules in the biotite. As olivine is an orthosilicate, silica will thus be made available, which will compensate for that taken up by the Fe_2O_3 in forming augite from the normative magnetite. As the amount of normative nephelite is considerable, however, it seems probable that this will not be entirely sufficient to change all the normative nephelite into albite, and that consequently some modal nephelite is actually present. It is possible also that the pyroxene contains some of the soda as acmite, which, having a ratio of SiO_2 to Na_2O of 4 : 1, will tend to lessen the amount of nephelite. The pyroxene present will then probably be composed largely of wollastonite and augite molecules, with a small amount of acmite."

It may be objected that the chemical analysis shows too small a percentage of silica (48.21 per cent.) to warrant the reference of the Cerrillos rock to a phase of andesite. Under the microscope, however, the feldspars are seen to be so far in excess of the ferromagnesian minerals as to rule the rock out of the basaltic group, according to our usual conception of the latter. The more peripheral portions of the same mass show a typical porphyritic andesite.

(*c*) *Augite Monzonite-Porphyry.*

This rock is similar to the "gabbro-porphyry" phase of the augite andesite, except that the orthoclase is about equal to the plagioclase in amount. It forms the large laccolithic masses of Santa Rosa, Santa Rosita, and Achavica Mountains, and one or two of the smaller hills.

The pale green augite is quite abundant, often in perfectly

bounded crystals, and contains inclusions of magnetite, apatite, and sagenite nets of rutile needles. The orthoclase and plagioclase crystals rarely have good boundaries, approaching the granitic habit in their development. The plagioclase varies from andesine through the more acid labradorites. Strongly pleochroic biotite is fairly abundant, but is notably inferior to the augite in amount. The color changes are from a straw yellow to a chestnut brown. Magnetite is fairly abundant, and apatite is present, often in large, thick, but short crystals. Very rarely a stray quartz grain is encountered. There is no groundmass, but occasionally a little interstitial filling of analcite (?) is seen.

In cases where the rock is somewhat decomposed a little calcite is observed, and considerable secondary quartz. Biotite may also occur as small shreds, especially about magnetite grains.

A specimen from Gray Hill differs from the above type in that the rock is porphyritic, the feldspar phenocrysts are nearly all orthoclase, and little or no biotite is present. The groundmass contains abundant rods of feldspar which appear to be plagioclase. Titanite occurs and much augite is present in the groundmass in the form of small shreds.

(*d*) *The Turquoise Matrix.*

A discussion of the augite andesite series would not be complete without a special consideration of the greatly altered form in which the turquoise deposits occur. In addition to being present throughout the whole field in connection with mineral veins and shear zones, this altered andesite forms several broad areas which are indicated on the map. The rock is yellow or white in color, and might be mistaken for an altered sandstone by the casual observer. Even in the hand specimen, however, remnants of feldspar phenocrysts are easily seen, and the true character of the rock readily discerned.

The rock has been microscopically and chemically examined by several observers interested in the turquoise deposits which occur in this altered phase at Mt. Chalchihuitl and Turquoise Hill, as well as in minor quantities at other localities in the district. In 1881 Professor Benjamin Silliman gave us a description from which I quote the following: "The rocks in which the turquoise occurs are seen, by the aid of the microscope and polarized light, in thin sections, to be plainly only the ruins, as it were, of crystalline

trachytes; they show fragments of feldspar crystals, decomposed in part into a white kaolin-like substance, with mica, slag and glassy grains, and quartz with large fluidal enclosures, looking like a secondary product." *

In Bulletin No. 42 of the United States Geological Survey, F. W. Clarke and J. S. Diller give a detailed microscopical and chemical discussion of "Turq uoise from New Mexico." From their paper I quote the following description of the country rock: "Under the microscope the rock is seen to be composed chiefly of feldspar, with a considerable amount of biotite, epidote, pyrite, and limonite, and some amorphous substance. It is somewhat microgranitic in structure, and the irregular, interlocking grains of feldspar vary in size from .01 to .8 mm. in diameter. Most of them are considerably kaolinized, so as to appear cloudy in ordinary light; but between crossed nicols the original outlines of the grains become more distinct. Their optical properties indicate that the feldspar is orthoclase, an opinion which is fully borne out by the subjoined analysis of the rock, which shows a remarkably large proportion of potash (analysis quoted below). The porphyritic crystals are generally Carlsbad twins with irregular outlines. There are occasionally small grains of fresh transparent plagioclase which has evidently resulted from alteration.

"The biotite of the rock occurs in noteworthy quantities, but is very unequally distributed. It is frequently aggregated in groups of scales and may be seen most abundantly in small cavities. It sometimes occurs intimately associated with the turquoise, but unlike the latter it is one of the primary minerals. The small quantity of quartz present is a secondary product, so intimately associated with turquoise as to suggest their genetic connection. Pyrite is scattered rather uniformly throughout the rock in small cubical crystals easily seen in the hand specimen. They are sometimes altered to limonite, but in other cases they have been completely replaced by pseudomorphs of epidote. The specimen of rock which was subjected to analysis probably contained an amount of pyrite rather greater than the average. One of the most important constituents of the rock, because of its very close association with the turquoise, occurs in the form of bright yellow grains. * * * Judging not only from the properties enumerated, but also from the percentage of lime in the rock, this mineral is in

* *Am. Jour. Sci.*, 1881, p. 70.

all probability epidote. It is evidently connected genetically with the turquoise, for it is almost uniformly found upon the border of the latter and is most abundant in its neighborhood. * * *

"The occurrence of this veritable orthoclase rock in the West is of special interest from the fact disclosed by recent investigations that in many of the rocks previously described as trachytes the predominating feldspar is plagioclase." *

A study of more than a dozen thin sections of the altered rock has convinced me of its original identity with the surrounding augite andesite. Where the rock is not too thoroughly decomposed, distinct traces of albite twinning of the feldspars can be made out. The continued alteration results in the obliteration of this twinning even before the crystal outlines are wholly destroyed. Twenty-five yards east of the eastern excavation of the turquoise mines of Mt. Chalchihuitl a specimen was secured in which the feldspars showed fairly well preserved twinning according to the albite law; and even right in the excavation a sample was collected less completely altered than the most of the rock, which showed abundant evidence of this form of twinning. From the pit of the main excavation on the west side of the hill a sample was gathered containing several veinlets of turquoise. A section of this specimen showed the albite twinning distinctly enough to leave no doubt as to the fact that most of the feldspar phenocrysts were plagioclase. A very small per cent. of the phenocrysts seen might be regarded as orthoclase. The orthoclase may be more abundant in the groundmass, but it does not appear so. The plagioclase was not secondary, but was profoundly altered with crystal outlines yet remaining. A few yards farther west, away from this altered zone, the rock shows abundant fresh plagioclase, as the chief feldspar.

Of the large number of specimens gathered by me from the excavations themselves, from the vicinity of the mine, and in the adjoining country, there was none that would be called a trachyte, and I cannot doubt that the bulk of the rock in which the turquoise occurs was, in its unaltered state, identical with the andesitic rocks of the rest of the region. It seems hardly possible that the analysis given by Clarke and Diller can represent the usual character of the rock. So large a percentage of potash (11.18 per cent.) is extraordinarily high, even for a trachyte, and demands a rock very

* Bull. U. S. Geol. Surv., No. 42, pp. 43, 44.

largely composed of orthoclase, wholly unlike anything found in the Cerrillos region by the writer. The petrographical description of the rock by Clarke and Diller shows the feldspars to be "considerably kaolinized, so as to appear cloudy in ordinary light." Under these conditions we should expect the rock to lose more or less of its potash, so that the high percentage is yet more difficult to understand.

Aside from the observations on the feldspars, my own conclusions from the study of these rocks did not differ materially from those quoted above at some length. Biotite was occasionally seen in irregular patches, sometimes largely altered to chlorite. Very rarely remnants of the augite were visible. It is noteworthy that this mineral is entirely gone in specimens which retain the feldspars fairly well preserved. Magnetite was rarely to be seen, while apatite was quite uncommonly noted. In the groundmass distinct plagioclase rods were discernible in one instance, but kaolinization obscured the whole mass as a rule. Pyrite, limonite, and epidote occur. Chalcedonic quartz fills irregular cavities in the rock at Mt. Chalchihuitl, while quartz in crevices and veinlets is common. In some cases these quartz veins are crushed, showing that the shearing had not ceased when the veins were formed. This crushing is also discernible in the feldspars at some localities.

The amorphous mineral referred to by Clarke and Diller is probably fluorite, as I find an isotropic mineral which appears to be fluorite fairly common in the rock with the turquoise in the main excavation at Mt. Chalchihuitl. In the excavation on the eastern side of the hill there is considerable tourmaline, from pale violet to deep blue in color, occurring as irregular fragments as a rule, but also as small, fairly well-bounded crystals.

Of the chemical analyses given below, No. 1 represents the fresh, coarse-grained variety (gabbro-porphyry) of the augite andesite from Mt. McKensie, a mile north of Mt. Chalchihuitl. While it cannot be said that this analysis represents the original fresh rock which in its altered phase contains the turquoise, the mineralogical evidence shows that there could have been no great difference in composition. Certainly this analysis must be closer to the original composition of the turquoise matrix than No. 2, which is the analysis given by Clarke and Diller for a somewhat altered phase of the matrix. No. 3 is a partial analysis of the kaolin of a completely kaolinized portion of the rock containing much pale blue tur-

quoise of earthy texture, also by Clarke and Diller. Except for the remarkable percentage of potash already referred to, Nos. 2 and 3 might well be derived from No. 1 by the processes of alteration which went on in the crushed zone about Mt. Chalchihuitl.

	No. 1.	No. 2.	No. 3.
SiO_2	48.21	56.68	52.38
Al_2O_3	17.96	16.62	} 33.49
Fe_2O_3	5.18	6.50	
FeO	4.47	.....	.....
MgO	4.11	.79	1.17
CaO	9.72	.59	trace.
Na_2O	3.68	1.03	.....
K_2O	2.99	11.18	.....
H_2O+	1.41	} 3.28	12.88
H_2O-	.21		
CO_2	none.	.....	.....
TiO_2	.84	.....	.....
ZrO_2	none.	.....	.....
P_2O_5	.58	.73	none.
SO_3	none.	.....	.....
S	none.	.....	.....
FeS_2	.....	2.21	.....
NiO	none.	.....	.....
MnO	.31	1.02	.....
BaO	.07	.....	.....
SrO	trace.	.....	.....
CuO	.....	trace, undet.	.....
Total.	99.74	100.63	99.92

That the 33.49 per cent. given for alumina and ferric iron in analysis No. 3 is largely alumina is indicated by the fact, noted in the original paper, that the kaolin itself was white, although the alumina from it was distinctly reddish with the iron.

The study of the turquoise itself is discussed in a subsequent section.

5. Olivine Basalt Series.

(*a*) *Olivine Basalt.*

Northwest of the Hills is a low volcanic crater and lava flow of olivine basalt. The rock is dull reddish-brown to black, and very vesicular.

Under the microscope the rock is seen to be composed of beautiful olivines surrounded by abundant plagioclase (basic labradorite) rods and shreds of nearly colorless augites. Magnetite is very abundant, and limonite stains give the rock its red color nearer the crater. Serpentine occurs as an alteration product from olivine.

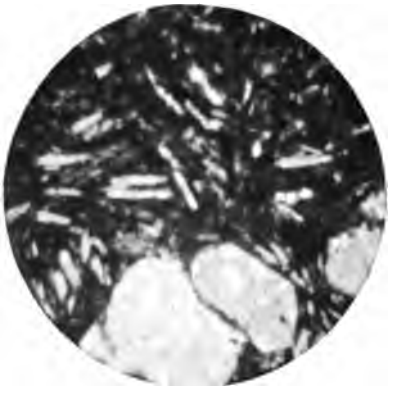


FIG. 1.—OLIVINE BASALT. (Between crossed nicols.)

FIG. 2.—LIMBURGITE FROM MT. CALVARY. (Between crossed nicols.)

(*b*) *Limburgite.*

The radial dykes associated with the above flow, as well as the rock of Mt. Calvary, belong to the feldspar-free limburgites.

The augites are extremely abundant, have a broadly lath-shaped outline most frequently, and are of the beautiful violet hue characteristic of the titanium-bearing variety. The olivine is fairly abundant, sometimes being more or less altered to serpentine. Biotite occurs in small amounts, magnetite is very abundant, apatite rare. There is sometimes seen what appears to be a little interstitial analcite.

In the more decomposed specimens calcite is abundant, and the olivine has largely gone over to serpentine. Occasionally irregular patches of secondary feldspar are seen. Chlorite was also noted.

The rock of Mt. Calvary is not markedly different from that in the dykes. The latter would be referred to the monchiquites according to Rosenbusch's classification. The fact that the rock of Mt. Calvary is compactly crystalline, and shows no evidence of having been formed on the surface, while there is no indication of any lava flow, would suggest that the hill was of laccolithic origin. Such an hypothesis, however, necessitates the assumption of two limburgites, closely similar in character, of widely different ages, with an intermediate (in time) flow of a typical basalt, rich in feldspar. While not impossible, this appeals to one as rather improbable. On the other hand, to regard this hill as the neck of a volcano of more recent age than the basalt volcano to the southwest, forces one to assume that a crater and flow existed at a higher level than the basalt flow, and that they have been completely eroded, both of which assumptions seem to be contradicted by the field relations. If the hill itself represent a small overflow from a dyke or other conduit of the same age as the limburgite dykes, it is difficult to understand how the rock it so dense and hard, while the older overflow of basalt is extremely vesicular.

The Turquoise.

The turquoise of the Cerrillos Hills has been described at some length by Clarke and Diller, and early attracted the attention of geologists to the region. The gem occurs in veins throughout the sheared and altered zones of the augite andesite, and as little nodules in streaks of kaolin filling crevices in the rock. The color varies from green through greenish-blue to pure sky blue. As stated by Clarke

and Diller: "The dark green nodules often shade off to nearly white at the center. * * * Many of the specimens are seamed or streaked by limonite, which has been derived from accompanying pyrite; and the latter mineral occasionally is found, bright and unaltered, inclosed completely in masses of clear blue turquoise." * Streaks of white kaolin, or kaolin slightly colored by limonite, are also common, destroying the value of much of the material.

Concerning the optical properties of the turquoise from this locality, Clarke and Diller write as follows: "Although deeply colored in the hand specimens, the thin sections appeared almost clear and transparent. Between crossed nicols the deep blue and green forms were seen to be composed of minute grains or short, thick fibers, but in the paler varieties the fibrous structure was more pronounced. The optical properties of both grains and fibers are the same throughout. They are all weakly doubly refracting, but have a rather high refractive index. The finely granular portions have a pale bluish aggregate polarization, less intense than that of chlorite, but when the mineral is distinctly fibrous it polarizes like some forms of serpentine, with light colors of the first order. The fibers are somewhat bent and interwoven, but lie approximately in the same direction. Each fiber becomes dark when parallel to the principal section of either of the crossed nicols, indicating that they must crystallize according to the quadratic, hexagonal, or rhombic system, instead of in one of the inclined systems, as was the case with the fibers studied by Bücking in the turquoise of Fresno County, California.

A section was prepared of a distinct vein of pale green turquoise, which showed that the fibrous structure is directly across the vein perpendicularly to its walls. Small fissures, running into or across the veins, have the fibers of turquoise arranged perpendicularly along their sides, just as serpentine arranges itself along fissures in olivine. Sometimes the fissures are minute and curved; but the resulting arrangement does not simulate the radial fibrous or spherulitic stucture described by Bücking as found in the turquoise of California, Nevada and elsewhere."

A study of a number of thin sections of the turquoise served to confirm, in the main, the observations above recorded. It will be seen, however, that the radial arrangement of the fibers was frequently noted, while the extinction of these fibers was found to be apparently slightly inclined, rather than parallel.

* *Ibid.*, p. 39.

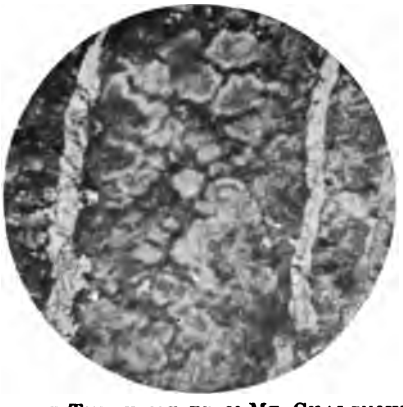


FIG. 1.—VEINLET OF TURQUOISE FROM MT. CHALCHIHUITL, SHOWING THIN SEAMS OF PROBABLE FLUORITE ON EACH SIDE SEPARATING THE TURQUOISE FROM THE MATRIX OF ALTERED ANDESITE SHOWN AT THE EXTREME RIGHT AND LEFT. (Ordinary light.)

FIG. 2.—TURQUOISE FROM MT. CHALCHIHUITL IN RIGHT HALF OF FIGURE, IN CONTACT WITH MATRIX SHOWN AT THE LEFT. THE INTERSTITIAL ISOTROPIC MINERAL, PROBABLY FLUORITE, IS REPRESENTED BY THE BLACK AREAS IN THE RIGHT HALF OF FIGURE. (Between crossed nicols.)

Under the microscope the turquoise is frequently seen as thin seams or stringers running throughout the rock. As a rule these seams are formed of more or less nearly rounded aggregates of the turquoise, sometimes packed closely together, the intervening spaces also being filled in part with turquoise; while in other cases these rounded aggregates are not so closely packed, and an isotropic mineral, probably fluorite, helps to fill in the interstices. Limonite and epidote may also appear in the latter association. This peculiar structure of the turquoise is shown in Plate T, Figs. 1 and 2; also Plate U, Fig. 1; which represent seams of the gem occurring in the altered andesite of Mt. Chalchihuitl.

Each one of these rounded aggregates is seen to be composed of fine, thread-like fibers, radiating outward from the center of the mass, giving a true spherulitic structure. In some cases these spherulites also exhibit concentric, shell-like layers, more or less distinctly developed. Most frequently these spherulites have a dull, earthy gray center, outside of which is a lighter area, while the extreme outer border appears decidedly darker in cases. The dull gray center often appears nearly or quite structureless, but the spherulitic arrangement of the fibers is well shown throughout the surrounding light band. The interstitial filling, like the borders of the spherulites, may become quite dark and impure in appearance.

In some instances the turquoise is more massive, and the spherulitic structure very imperfect, or wholly wanting. When the latter is true, the fibers run across the vein, perpendicular to the walls being approximately parallel to each other.

The fibers, in both the spherulites and in the seams where the fibers are nearly parallel, appear to extinguish at a low angle. The determination of this point is not easy, but wherever the evidence was at all plain, there seemed to be little doubt of the inclined extinction. The polarization colors are generally pale gray-blue or straw yellow, the mineral being rather weakly doubly refracting. When a section of the more massive variety is cut parallel to the walls of the vein, *i. e.*, perpendicular to the fibers, the microscope shows a fine, granular aggregate, with aggregate polarization.

Reference has already been made to the occurrence of the isotropic mineral most closely resembling fluorite, which is associated with the turquoise. The method of its occurrence is well shown in Plate T, Fig. 1. Here the fluorite (?) is seen as small seams on

either side of the vein of turquoise, separating the latter from the matrix of altered andesite, and also less distinctly as an interstitial filling between the spherulites of turquoise in places. In Plate U, Fig. 1, one of the seams of fluorite (?) is seen to widen out to much greater proportions, while the occurrence of this mineral as an interstitial filling is better shown.

The appearance of the turquoise, as seen in the above relations, strongly suggests the crystallizing out of the gem from solutions in small fissures, excluding the molecules which later formed the fluorite. If, as is believed, these solutions represented in part the original apatite scattered throughout the country rock, the occurrence of fluorite would be quite natural. The evidence does not seem to me to suggest the formation of the turquoise by alteration of vein apatite formerly occupying these same fissures.

No cases of veinlets of turquoise with transverse fibers penetrating larger seams of the same gem, such as were reported by Clarke and Diller, were seen in the sections examined. Their occurrence would not be unnatural, no matter what the origin of the turquoise might be, since they would represent recrystallization of the mineral in fissures opened in the older veins. Occurrences of this sort have been noted in fibrous serpentine, even where the latter did not represent replacement of olivine.

As noted in Part I. of this report, it seems most likely, in view of facts already referred to, that the turquoise is the original occupant of the fissures in the altered rock, rather than a secondary replacement of vein apatite. The fact that no evidence of vein apatite has ever been found in the region, and that the form of the turquoise in no case suggests its former presence, while of only negative value, nevertheless throws some doubt on the vein-apatite hypothesis. On the other hand, the appearance of the turquoise under the microscope, the manner of its occurrence in the veins and its relations to the associated fluorite (?), as well as the effectual disappearance of the usual content of apatite from the rock in the vicinity of the turquoise deposits, seem to favor the simpler method of origin: — that the gem is a secondary product, but the original occupant of the vein, — the alumina and phosphoric acid having been derived from the feldspar and apatite of the country rock, the copper being brought in from the same source (possibly indirectly) as the copper found in neighboring mineral veins. It seems not unlikely that this alteration of the rock was facilitated by hot solu-

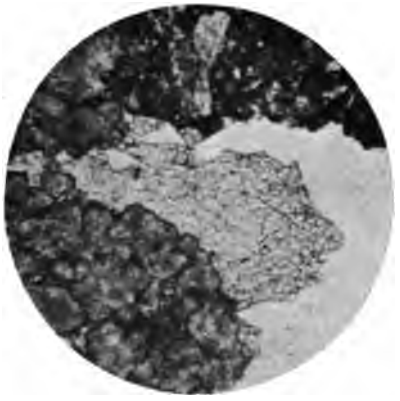


FIG. 1.—TURQUOISE FROM MT. CHALCHIHUITL (lower left hand part of figure) SHOWING UNUSUALLY LARGE AMOUNT OF FLUORITE (center of figure) AND PORTION OF MATRIX CONTAINING PLAGIOCLASE FELDSPARS (upper part of figure). (Ordinary light.)

FIG. 2.—TURQUOISE FROM TURQUOISE GULCH, COLORADO, SURROUNDING CORRODED QUARTZ CRYSTALS. (Between crossed nicols.)

tions and vapors rising along the crushed and fractured zone. The presence of tourmaline, copper, pyrite, etc., is suggestive of some such action. Further reference to the origin of the turquoise appears in Part I. of this report. (The brief statement regarding the origin of the turquoise given at the very beginning of Part I. is misleading, and has been corrected in "Addenda et Corrigenda.")

Through the courtesy of Mr. George F. Kunz, of New York City, I was enabled to examine specimens of turquoise from near Silver City, New Mexico, and from Saguache County, Colorado, and through the kindness of Mr. N. W. Lloyd, of Pearce, Arizona, I was favored with a suite of specimens from this locality. While only small fragments of the matrix adhered to the specimens examined, it seemed evident that the veinlet from Silver City, New Mexico, filled a small fissure in quartzite. The turquoise from this locality was in part fairly massive, but portions of the vein showed a tendency toward the collecting in small, rounded aggregates. So far as I could determine the radial arrangement of the fibers in the rounded masses was very poorly if at all developed.

In the specimens from near Pearce, Arizona, the gem is seen to be very pure and massive, the entire sections showing little but pure turquoise. Sections were obtained both parallel and perpendicular to the walls of the vein, and when examined under the microscope showed a beautiful development of the spherulitic structure. The spherulites are not isolated as in the Cerrillos gem, but appear without definite borders, the whole mass being composed of imperfect but distinctly spherulitic aggregates of radial fibers in the finely granular "groundmass" — all of turquoise.

The gem from Saguache County, Colorado, shows a rather peculiar mingling of the radial arrangement of the fibers, and the arrangement perpendicular to the walls of the vein. For parts of the vein show many parallel fibers, perpendicular to the vein wall, and extinguishing together, while mingled with them are rounded areas with an imperfect development of the radial arrangement. In other parts of the vein the spherulitic structure is more pronounced, but is never so finely developed as in the Cerrillos or Pearce examples. A section of the Colorado material parallel with the walls of the vein showed a number of hexagonal cross-sections of quartz crystals, sometimes more or less corroded. It would appear that the quartz crystals formed on the walls of the

open fissure, projecting out into the cavity, while the turquoise formed later. A section parallel to the walls would then cut these crystals at right angles to the axis *C*, showing the hexagonal outlines noted. Plate U, Fig. 2 shows an example of such an occurrence.

Several analyses of the Cerrillos turquoise have been made, and are recorded below. The earliest one of which we have mention is that given by Dr. Oscar Loew in 1875,* and is quoted as No. 1 in the following table. Nos. 2 (bright blue) 3, (pale blue, greenish cast), and 4 (dark green), are quoted from the paper by Clarke and Diller,† and were made in the Washington laboratory of the United States Geological Survey. No. 5, given by Church for the Persian gem; No. 6, by G. E. Moore of turquoise pseudomorphous after apatite, from Fresno County, California; No. 7, by Nikolaieff of the mineral from Karalinsk in the Kirghiz Steppes; and No. 8, by Penfield of turquoise from Lincoln Co., Nevada, are tabulated for comparison.

ANALYSES OF TURQUOISE.

	1	2	3	4	5	6	7	8
H_2O	18.85	19.80	19.60	18.49	19.34	19.98	18.60	19.38
Al_2O_3	29.17	39.53	36.88	37.88	40.19	35.98	35.79	35.03
Fe_2O_3	.....	.....	2.40	4.07	.....	2.99	3.52	1.44
P_2O_5	29.57	31.96	32.86	28.63	32.86	33.21	34.42	34.18
CuO	4.04	6.30	7.51	6.56	5.27	7.80	7.67	8.57
SiO_2	12.57	1.15	.16	4.20	.....	.....	.....	.....
FeO	4.35	.....	.....	.....	2.21	.....	.....	.....
CaO	1.61	.13	.38	Undet.	.....	.....	.....	.....
MnO	.....	.....	.....	.....	.36	.....	.....	.....
Insol.	.....	.....	.....	.....	.....	.....	.....	.93
Total	100.16	98.87	99.79	99.83	100.23	99.96	100.00	99.53
Sp. gr.			2.805	2.426–2.651 (Blake)‡	2.75	2.798–2.815	2.89	2.79

Concerning the large percentage of silica in No. 1 Dr. Loew says that he was very careful to separate the turquoise from all adhering trachyte, so that the silica must have occurred in the gem itself. Clarke and Diller say the same regarding the silica in No. 4. They consider the small amount of silica in No. 2 to be due to admixed rock from which the turquoise could not well be perfectly freed. The analysis of No. 2 is not complete because sufficient material

* Report Chief of Engineers, 1875 Part II., p. 1028.

† Bull. U. S. G. S., No. 42, p. 40.

‡ For similar specimens.

was not available without the destruction of valuable specimens. In a paper referred to above* Silliman records 3.81 per cent. of copper, which corresponds to 4.78 CuO, but gives no other quantitative data.

Clarke and Diller discuss the analyses in some detail, and on the evidence furnished by them suggest the following formula for normal turquoise, $Al_2HPO_4(OH)_4$, considering the color due to the copper salt $2CuO, P_2O_5, 4H_2O$, which occurs merely as an impurity. The green varieties would then owe their color to added amounts of iron salts. Penfield, in his paper on "The Chemical Composition of Turquoise," † discusses these same and additional analyses, and reaches the conclusion that the copper and small amounts of iron are not present as impurities, but are essential constituents of turquoise.

Summary.

In conclusion we may note the close andesitic affinities of all the rocks of the region, if we except the basalts. The few exposures of older Cretaceous eruptives show a rock belonging to the mica andesite group, while the later Cretaceous breccias are largely composed of andesitic fragments. The earliest of the post-Cretaceous outbreaks was a typical hornblende andesite, which was soon followed by rocks of the augite andesite series. The evidence points to an andesitic magma which has been tapped off at widely distant intervals, not yielding notably different lavas. The basalts are of still later age, and the evidence points to two different eruptions of this basic series, the limburgite dykes being intruded subsequent to the outflow of the true basaltic lava, as shown in Part I. of this report.

The matrix of the turquoise is shown to be greatly decomposed andesite occurring along sheared zones. The turquoise occurs as an alteration product, the alumina and phosphoric acid being derived from the feldspars and apatite of the country rock, while the copper was brought in by solutions that were probably active in effecting the decomposition of the rock. The microscopic features of the turquoise are discussed.

* *Am. Jour. Sci.*, 1881, p. 70.

† *Am. Jour. Sci.*, Vol. X., 1900, pp. 346–350.

ADDENDA ET CORRIGENDA.

Part I. General Geology.

Page 303, line 15.—It should be added that the photographs from which Figs. 7, 10 and 12 were reproduced, were taken in connection with this earlier work on the University Survey.

Page 306, line 29, *et seq.*—For this paragraph read: "(*g*) The turquoise occurs in altered portions of the andesite, and was formed as a secondary product from the alteration of the country rock, the alteration being caused by, and the copper in the turquoise probably contributed by, heated solutions (and vapors) rising along lines of fracture in the rock."

Plates C and K.—From photos by C. H. Dague, of Cerrillos.

Plate I.—Drawn by R. B. Johnson from photo by E. F. Bennet, of Cerrillos.

Part II. Palæontology.

Page 193, line 4.—As suggested by Mr. T. W. Stanton, *Aucella strongi* is an *Inoceramus* probably referable to the section or subgenus *Volviceramus*.

Page 201, line 25.—On comparing my specimens referred to his *Tritonium kanabense*, with the type, Mr. Stanton expressed his conviction that the forms were not identical. He says: "The type of the species, which is the only one I have seen, as compared with your specimens, has straighter growth lines, straighter and relatively more prominent costæ, and slightly different spiral sculpture. It also has two important features of which I see no trace on your specimens, viz., a strongly dentate outer lip, and occasional prominent varices representing earlier apertures."

As it has been impossible for me to secure the opportunity of studying Mr. Stanton's types at the National Museum, I can only suggest the specific name "*cerrillosensis*" to designate this form in case it proves specifically distinct from Mr. Stanton's type. The figure of the latter, given in Bulletin 106 of the U. S. G. S., is so unsatisfactory that the reference seemed justifiable.

THE SANITATION AND PROPOSED SEWERAGE SYSTEM OF HAVANA, CUBA.

By A. E. CARTER, Assoc. Mem. Am. Soc. C. E.

When the United States Army of Occupation entered Havana in 1898, it found that sanitary work had been very much neglected. Although the unsanitary conditions can be partially attributed to the protracted war, it was apparent to any person who had some knowledge of sanitation and cleanliness, that the training of the native people of this city had been neglected along lines of sanitary engineering necessary for good health, especially in a city situated in the tropical zone.

The streets were covered with filth, such as garbage and house refuse, which varied in depth from one half inch to three or four inches and had been accumulating for years. The first duty of the Volunteer Engineer Corps, after their arrival, was to direct the work of renovating the streets, parks, public buildings and vacant grounds at least to such an extent as would make the city inhabitable for the representatives of our government.

Havana is situated between the Gulf of Mexico on the north and Havana Harbor on the east. A ridge divides the city into two watersheds, one draining into the gulf, the other into the harbor. Havana has no regularly designed sewerage system. In some parts of the city, drains of coral rock with stone slab coverings have been laid upon the natural soil. They are inefficient and inadequate to carry off the storm water of the heavy rains. The overflowing of streets and the flooding of house floors are common occurrences. These drains also receive sewage from dwellings and the overflow from cesspools, and discharge the same at the water's edge of the gulf or harbor, as the case may be. There being no lining in the bottom of the drains, a large per cent. of the sewage soaks into the soil. The interior being rough, angular and without proper grades, a large portion of the filthy matter is retained, putrefying and giving off, through the untrapped storm water inlets, odors that are not only disagreeable but are more or less detrimental to health. (The writer has observed several inlets in the bottom of which the sewage had no perceptible velocity.) In some of the suburban districts there are no sewers or drains, the gutters and small streams having served to carry away the liquid waste.

Prior to the building of the existing "sewerage system," if it may be called such, the sewage of the old part of the city was discharged into cesspools beneath the floors of the buildings. Under the direction of the engineer corps many of these cesspools were cleaned by removing from each, quantities of sludge varying from twenty-five to seventy-five cart loads; the liquid sewage had filtered away through the porous coral rock which underlies the city. Previous to the installation of the existing water supply, water was used for domestic and other purposes from wells sunk in the porous rock, which in many instances were near cesspools.

At present only a small per cent. of the liquid wastes is discharged into the "sewers," the cesspools still serving the purpose for which they were built. Also, there are, adjoining living quarters, open fixtures and toilet rooms connected with these cesspools and without any provision for ventilation.

Under these existing conditions, with yellow fever claiming several hundred lives each year, tuberculosis being very prevalent, and smallpox often visiting the city, all stimulated by unsanitary conditions, our government officials in charge of affairs were prompted to insist that the city of Havana should have an efficient sewerage and drainage system to complete and maintain the sanitary work inaugurated by them.

Mr. Samuel Gray, consulting engineer, of Providence, Rhode Island, was engaged to make a careful and thorough examination of the conditions, devise a method of sewering and draining the city and determine the most practical and thorough means of disposing of the sewage. One of the most important problems that presented itself was its practical and economical disposal. After considering irrigation and filtration, chemical precipitation, and the septic system, Mr. Gray concluded that conditions were in favor of disposal by dilution. It was then necessary to locate a point in the gulf where sewage could be discharged with an assurance that it would not be carried by winds or ocean currents back to the shore around the city, nor into the harbor. After spending considerable time in making observations with floats, and studying the different points at which sewage could be concentrated practically and economically, a point about one mile northeast of the city was selected. Here the sewage will be discharged six hundred feet off shore in twenty-five feet of water.

The meteorological records of the last twenty-six years show that during the severest storms, average rates of rainfalls of two and one tenth, two and four tenths, two and thirty-two hundredths, two and seventy-four hundredths, and three and seven hundredths inches per hour have been recorded. These were not storms of long duration; such downpourings of rain usually continue only a few minutes. As the streets will be paved and practically all the area of the blocks is covered by buildings or paved patios, a very large per cent. of the storm water may be expected to run off. Mr. Gray recommended that a rate of two and one half inches of rainfall per hour be assumed in designing the new drainage system.

The source of water supply is Vento Springs, situated about eight miles south of the city, and the supply is abundantly sufficient for many years to come. The estimated consumption of water is one hundred and twenty-five gallons per capita per day. The assumed consumption for the purpose of designing the new system was one hundred and fifty gallons per capita per day, plus fifty per cent. for the maximum, or two hundred and twenty-five gallons per capita per day. In addition to the above assumption, one hundred and fifty gallons per acre per day is allowed for ground water reaching the sewers.

The present population of Havana, according to the last census, is two hundred and forty-five thousand. In some parts of the city there are two hundred and forty-six people per acre, but the general average for the old part is about one hundred and twenty-five per acre. The average population in the suburbs is much less than this.

The maximum rate of discharge of sewage for the city, when it will have a population of six hundred thousand inhabitants, has been estimated to be seven hundredths cubic feet per second for the old part, and twenty-eight thousandths cubic feet per second in the suburban districts.

The object sought, that of removing storm water from the streets and sewage from the houses, stores, hotels and other buildings could be accomplished by either of two systems, namely, the "Combined" or the "Separate Systems." The Combined System is a single sewer or drain carrying both storm water and sewage, When pumping is necessary, as it will be here, automatic regulating devices are required to prevent the storm water from reaching

the pumping station. These regulating devices could not do more than prevent a portion from entering the pump well, and would also cause sewage to be carried out through the storm water outalls, which is one of the things to be avoided.

A combined sewer, to prevent surcharging and overflowing into the streets, would need to be very large where heavy rains occur. If a sewer is larger than is required to carry the sewage alone, it becomes necessary to flush it often during dry weather, as the large section will not remain clean with the flow of sewage alone.

The "Separate System" consists of a drain for storm water and a small sewer for sewage. In this system, if a drain becomes surcharged and overflows into the street, nothing is carried to the surface that did not come from there originally; moreover, the amount of flushing and pumping is very much reduced. In Havana, where large drains will be required, the Combined would probably be about as expensive as the Separate System. The latter was recommended by Mr. Gray for the new sewerage system for Havana. As the streets are very narrow, averaging about six or seven meters in width, it will be necessary to use the mininum width of trench excavation; this will be accomplished by crossing the drain over the sewer in traversing each block, thus placing a large portion of the drain in the sewer trench. The centers of the sewers are to be not less than one and seven tenths meters, and the crowns of the drains are to be not less than one meter below the street surface.

The drains will be constructed according to the following sections: Drains from twelve to twenty inches in diameter inclusive are to be of sewer pipe; those of diameters of twenty-four to thirty inches inclusive are to be four-inch rings of brick laid in cement mortar; those of diameters greater than thirty inches to be of concrete with brick inverts. There will be a few exceptions where rectangular sections with inverted arch bottom will be used instead of the standard circular section. The minimum velocity in drains and sewers is to be three feet per second. In those parts of the city where the streets are from five to seven meters wide, combination manholes will be used, thus making one opening into the street surface serve both drain and sewer. Manholes are located at street intersections; also an intermediate one if the block has a greater length than eighty meters, and the sewer has a slope less than fifteen per thousand.

Inlets are so located that storm water will not flow in the gutter further than across one block. District drains converge into larger drains which in number, are governed by the number of drainage areas. These larger drains terminate in flanged cast-iron pipe outfalls discharging off shore in ten feet of water.

The total sewage of the city will be collected at the foot of O'Reily Street, on the north shore of the harbor and about two thousand feet inland from the gulf coast. Here will be constructed two Sand Catchers. From these Sand Catchers two trunk or marginal sewers branch out — one, the north side marginal, sixty-two inches in diameter, the other, the east side marginal, seventy-six inches in diameter. The former will cross the northern point of the city and then follow the gulf coast; the second will follow the foot of the slope of the watershed adjacent to the harbor. These marginal sewers are interceptors which receive all the sewage from the district sewers.

The district sewers are designed to flow one half full, thus providing ample capacity to meet any emergency that is likely to occur. The minimum diameter for sewers is eight inches. The sections are circular, and are of the same construction as the drains, except that all sewers have a five-inch semicircular bed of concrete. The minimum slopes for line sewers are governed by the discharge, diameter and minimum velocity. The minimum slope for dead end sewers without automatic flush tanks is fifteen per thousand. The coefficient of roughness used for sewers and drains, less than twenty-four inches in diameter, is thirteen thousandths. The coefficient for sewers and drains whose diameters are twenty-four inches or more, those having brick inverts, is fourteen thousandths. Diameters for sewers and drains were determined by diagrams plotted by Kutter's formula. Discharges of storm water for drainage areas were determined by a curve plotted by McMath's formula, using areas for abscissæ and discharges for ordinates.

There is a low suburban district, relative to the north side marginal sewer, in the southwestern part of the city from which the sewage will be discharged into the marginal sewer by means of two sublift pumping stations. These pumping stations will be built below the street surface and each will contain a small centrifugal pump direct-connected to an electric motor, which will be operated automatically. The lift and discharge at these stations will be small.

The purpose of the two Sand Catchers at the foot of O'Reily Street will be to prevent any material, not carried in suspension from entering the two siphons that cross the harbor from this point. These Sand Catchers are two catch basins in duplicate whose bottoms are four feet and six inches below the invert of the north side marginal sewer, and each is ten feet in width. The wetted cross-section, when both are in operation, is sufficient to reduce the maximum discharge to a velocity of one foot per second, at which velocity all material not in suspension will be deposited.

The sewage will be carried from the catch basins to the pumping station on the east side of the harbor by two cast-iron siphons sixty inches in diameter. They will be laid in trench and concrete in the bottom of the harbor which attains a depth of fifty feet near the center.

There will be installed, in the pumping station, two submerged centrifugal pumps, each having a lift of twenty-five feet and a capacity of forty-six million gallons per day. These pumps will be driven by independent, condensing, triple expansion engines, direct-connected to vertical shafts of pumps. Water tube boilers of the horizontal type, with mechanical stokers and mechanical draft, will be installed. The station will contain independent engines for driving dynamos for lighting and power purposes, also a traveling electric crane and coal handling machinery. The sewage is lifted to the tunnel, which pierces the hill between the harbor and the coast east of El Morro. From the tunnel the sewage is carried in an open cut to the cast-iron pipe outfall.

The writer wishes to acknowledge his indebtedness to Mr. Gray for information obtained from his report for the proposed sewerage and drainage system of Havana.

ALUMNI AND UNIVERSITY NEWS.

SCHOOL OF CHEMISTRY.

General.— During the summer session of the university this year, the same courses in chemistry were given as during the summer of 1902, and by the same officers, but the number of students was greatly increased. The great advantages to be obtained, in having access to the resources of the Havemeyer Laboratories, have been appreciated by many besides the teachers for whom these courses were primarily organized. Many students, entering the schools of applied science with advanced standing, can now either make up or anticipate much of their laboratory work in chemistry, by attending the summer session, and so avoid conflict of hours during the regular session and, by this means, often save a term in obtaining their degree.

All of last year's graduates have obtained positions, and it has been necessary to answer many requests for chemists, during the past summer, by saying that we have none "out of a job."

Analytical Chemistry and Assaying.— In qualitative analysis the teaching force has been increased and strengthened by the appointment of two new tutors in analytical chemistry: Mr. H. T. Beans, formerly University Fellow in Chemistry, a graduate of the University of Nebraska, who has had considerable experience in teaching chemistry in Idaho, and Mr. C. H. Ellard, who was formerly assistant in qualitative analysis.

In assaying there is an increase of students even over last year, so that the class is divided into sections for both recitations and laboratory work during the first half-year.

The results of some of the work done in this laboratory during the past year were given in a paper on "The Reduction of Lead from Litharge in the Preliminary Assay, and the Advantages of an Oxide Slag," in the *Transactions of the American Institute of Mining Engineers* — October, New York meeting.

Quantitative Laboratory. — The capacity of this laboratory was increased during the summer by making eight additional desks from cupboards previously used for reagents, so that it now accommodates eighty-eight men; but, notwithstanding, it has been necessary to put ten students in quantitative at work in the organic laboratory on account of lack of room. During the second half-year, when the large section of mining engineers takes the places now occupied by the electrical engineers, the numbers will be even larger.

The only change in the staff has been the appointment of Mr. F. V. D. Cruser in place of Mr. J. L. Danziger, who resigned to take up technical work.

Professor Miller has been elected Chairman, and Dr. Sherman, Secretary, of the New York Section of the American Chemical Society for the year 1903–04.

The publications which have appeared since the last notice in the QUARTERLY are:

"A Study of the Quantitative Determination of Antimony." By Louis A. Yoütz. SCHOOL OF MINES QUARTERLY. Part I., April, 1903; Part II., July, 1903. Also *Zeitschrift für Anorganische Chemie*, Vol. XXXV., p. 55.

"The Gravimetric Determination of Mercury and its Separation from Arsenic, Antimony and Copper." By C. J. Pretzfeld. *Journ. Amer. Chem. Soc.*, February, 1903.

"The Volumetric Determination of Bismuth as Molybdate and its Separation from Copper." By H. S. Riederer. *Journ. Amer. Chem. Soc.*, September, 1903.

"On the Reduction of Molybdenum by Zinc and the Ratio of Bismuth and Molybdenum in Bismuth Ammonium Molybdate." By E. H. Miller and Henry Frank. *Journ. Amer. Chem. Soc.*, September, 1903.

"A Rapid Method for the Determination of Arsenic in Arsenopyrite." By J. L. Danziger and W. H. Buckhout. SCHOOL OF MINES QUARTERLY, April, 1903.

"The Influence of Atmospheric Oxidation on the Composition and 'Analytical Constants' of Fatty Oils." By H. C. Sherman and M. J. Falk. *Journ. Amer. Chem. Soc.*, July, 1903.

"A Modification of the Babcock-Blaisdale Viscosity Test for Olive Oil." By Herbert Abraham. *Journ. Amer. Chem. Soc.*, September. 1903.

"The Viscosity of the Soap Solution as a Factor in Oil Analysis." By H. C. Sherman and H. Abraham. *Journ. Amer. Chem. Soc.*, September, 1903.

The following will appear shortly:

"The Influence of Diet, Muscular Exertion and Loss of Sleep upon the Formation of Uric Acid." By H. C. Sherman. *Journ. Amer. Chem. Soc.*

"An Index to the Literature of Thorium, 1828–1902." By C. H. Joüet. In the publications of the Smithsonian Institution. (Delayed by strike in Government Printing Office.)

The following researches are nearly completed:

Professor Miller and Mr. J. T. Thompson: "On the Conversion of Lead Sulphate to Barium Sulphate and a Method for the Determination of Sulphur in Lead Slags."

Professor Miller and Mr. Cruser: "On the Methods for the Determination of Molybdenum in Steel." The methods are tested on samples of steel containing besides molybdenum, tungsten and vanadium, and also on other molybdenum alloys furnished by Dr. Mathews of the Crucible Steel Company.

Dr. Sherman: "The Determination of Nitrogen in Organic Materials."

Mr. Beatty, University Fellow in Chemistry, has been obliged to postpone his research on the chromicyanides on account of ill health, but will continue this work next year. The results of the preliminary work, showing a large number of new chromicyanides, were exhibited at a meeting of the Society of Chemical Industry last March.

Organic Chemistry. — Courses 33 (Organic Chemistry, General Laboratory Course) and 35 (Organic Chemistry, General Lecture Course) have been united in a single course known as Chemistry 21, Organic Chemistry, General Course. This is a required course for all fourth-year chemists, also open to candidates for the A.M. degree, and includes

five hours' lecture room exercises, and from six to fourteen hours laboratory work per week.

Since the last report in the QUARTERLY the following papers have been published by the Organic Laboratory:

1. "On the Production of the Imides of Succinic and Glutaric Acids by the Partial Hydration of the Corresponding Nitriles." By M. T. Bogert and D. C. Eccles. *Journ. Am. Chem. Soc.*, XXIV., 20–25.

2. "The Synthesis of Alkylketodihydroquinazolines from Anthranilic Nitrile." By M. T. Bogert and W. F. Hand. *Journ. Am. Chem. Soc.*, XXIV., 1031–1050.

3. "Normal Heptyl Thiocyanate and some new Alkyl Esters of Dithiocarbamic Acid." By M. T. Bogert. *Journ. Am. Chem. Soc.*, XXV., 289–291.

4. "The Synthesis of Alkylthioketodihydroquinazolines from Anthranilic Nitrile." By M. T. Bogert, H. C. Breneman, and W. F. Hand. *Journ. Am. Chem. Soc.*, XXV., 372–380.

5 "p-Aminobenzonitrile." By. M. T. Bogert and L. Kohnstamm. *Journ. Am. Chem. Soc.*, XXV., 478–483.

6. "Review of Holleman-Walker's" A Textbook of Organic Chemistry." *Journ. Am. Chem. Soc.*, XXV., 655. By M. T. Bogert.

7. "Note on the Mononitro-o-phthalic acids." By M. T. Bogert. *Journ. Am. Chem. Soc.*, XXV., 767–770.

8. "3-, 5-Bibron-2-Aminobenzoic acid; its Nitrile and the Synthesis of Quinazolines from the latter." By M. T. Bogert and W. F. Hand. *Journ. Am. Chem. Soc.*, XXV., 935–947.

9. "The Production of Anicic Acid by the Oxidation of Aniseed Oil." By M. T. Bogert and Carl H. Zieme. SCHOOL OF MINES QUARTERLY, XXIV, 500-509.

10. "Review of American Chemical Research." By M. T. Bogert. *Journ. Am. Chem. Soc.*, XXIV., 21–27, 87–91, 164–171, 224–230, 303–310, 354–361, 528–532; XXV., 4–7, 74–78, 123–131, 167–178, 227–229, 274–278, 311–322, 361–365, 464–467.

11. "Review of Berthelot's Les Carbures d'Hydrogene." By M. T. Bogert. *Journ. Am. Chem. Soc.*, XXIV., 289–292.

12. "On the Relation of the Chemical Constitution to the Physiological Action of Certain Modern Anæsthetics." By Wolfram E. Dreyfus, Ph.D. *The Chemical Pub. Co.*, Easton, Pa.

13. "The Action of Isovaleric Aldehyde upon Antipyrine." By David C. Eccles. *Journ. Am. Chem. Soc.*, XXIV., 1050–1052.

14. "3-Nitrophthalyl Chloride and its Action with Ammonia and with Aromatic Amines." By Victor J. Chambers, Ph.D. *Journ. Am. Chem. Soc.*, XXV., 601–612.

Paper No. 8 in the above list was read at the summer meeting of the American Chemical Society, held last June at Cleveland, O. At the December meeting of the New York Section of the American Chemical Society Mr. Hal T. Beans presented the results of his work with m-Aminobenzonitrile, and a paper on the subject will appear shortly.

Other investigations are in progress in the Organic Laboratory, and results will be communicated later.

Laboratory of Industrial Chemistry. — Applicants for Chemistry 26 are now required to take Chemistry 7 as a prerequisite, in consequence of which the usual number of college students taking this course has

been reduced, but the advantage of a thorough grounding in qualitative analysis has been felt necessary for some time past for students in this course.

A new course has been added (Chemistry 39) for the fourth-year electrical engineers. This is a practical course in electrochemistry under Mr. Tucker, who has gotten out a set of printed notes, published in the SCHOOL OF MINES QUARTERLY for July.

The necessity of such a course for electrical engineers has been realized for some time past, owing to the increasing demand for electrochemists.

L. H. Dempwolf, Jr., published the results of his research on phosphates in the *Journal of the American Chemical Society* for August.

Mr. Tucker, in conjunction with E. H. Holmes, 1904, has undertaken an investigation of arc light electrodes.

The course in chemical microscopy, Chemistry 34, given by Professor Pellew for the first time last year to the regular second-year chemists, has opened this year with a dozen students, including several specials. To accommodate this increased class, the Dyeing Laboratory has been equipped with microscope desks, where the work can be done this year, although not without considerable inconvenience. If the numbers increase next year at all proportionately, the class will probably have to migrate to another building.

Columbia University Chemical Society. — The first meeting of the year of the Columbia University Chemical Society was held at Havemeyer Hall on the evening of October 15. Dr. Harvey W. Wiley, of the U. S. Agricultural Department, came on from Washington and gave an extremely interesting address, illustrated with many lantern slides, upon the work done under his supervision in Washington, during the last year, in testing the effects of food preservatives of various kinds upon digestion.

At the conclusion of his entertaining and instructive lecture, Professor Henry F. Armstrong, of London, made a few remarks to the audience, calling their attention to the great value to the whole civilized world of this work of Dr. Wiley's, and comparing the original work of American laboratories during the last few years very favorably with that done in Germany.

After this the large audience, which included many prominent alumni, and representatives from the chemical societies of the city, as well as from the King's Crown, the Deutscher Verein, the Philharmonic Society, the Glee Club, and many other student organizations, were entertained by the Chemical Society at a Kneipe, in honor of Dr. Wiley, held in the officers' lunch room in University Hall. Professor Pellew acted as toastmaster, and the following programme was carried through with great enthusiasm and good-fellowship.

PROGRAMME.

1. The Guests of the C. U. Chemical Society.
   Song, "Amici."
2. Our Guest of Honor, Dr. Wiley.
   Song, "A Famous Yankee Chemist."
3. The Faculty — Quite a Few of Them.
   Song, "The Faculty Song."

4. The Faculty — A Saving Remnant.
   Song, "Van Am."
5. The Columbia Y. M. C. A.
   Song, "The Song of the Good Boys."
6. Our Football Team.
   Song, "Mr. Morley."
7. Our Former Heroes.
   Song, "Glory, Glory for Columbia."
8. Our Alumni.
   Song, "Auld Lang Syne."
9. Dear Old Columbia.
   Song, "Sans Souci."
10. Our Alma Mater.
    Song, "Stand, Columbia."

On Friday November 13, Dr. Hans Goldschmidt from Essen, Germany, delivered an extremely interesting address upon alumino-thermics before a very large and representative audience of professional chemists and engineers, and of representatives of the various scientific societies of this city, as well as of the members of the Columbia University Chemical Society. The lecturer was introduced by G. H. Pickard, '04 Science, president of the society, and, in the course of his lecture, he made a large number of brilliant experiments illustrating the extraordinary amount of concentrated heat which he could obtain by means of his new process, and the many important applications for which it could be used. The large lecture room in Havemeyer Hall was completely filled by the audience, which was very enthusiastic over the success of the lecture.

The next meeting of the Columbia University Chemical Society was held on Thursday, November 19, at the Harlem Casino, at seven o'clock. After dinner, the guest of the evening, Dr. Leo Baekeland, of Yonkers, addressed the society upon the subject of "Photographic Chemistry" in which he is an acknowledged expert.

The third meeting of the Chemical Society was held on Friday, December 11, at the Harlem Casino at seven o'clock, where a large number of members assembled to hear Professor Edward Hart, of Lafayette College, Easton, Pa., deliver a very interesting address upon "Chemical Manufacturers," a subject in which, as the president of the well-known firm of Baker and Adamson, manufacturing chemists, he takes a keen personal interest.

DEPARTMENT OF MINERALOGY.

Mr. John Crawford, Jr., a graduate of Princeton University, and for three years a student in mineralogy and chemistry under Professor Cornwall, has been appointed assistant in mineralogy for 1903–04, and Mr. Louis G. Michael, graduate and acting instructor in mineralogy of the Michigan Agricultural College, has been appointed University Scholar in Mineralogy.

The old courses, Mineralogy 1, 2 and 4, given hitherto in three terms, have been consolidated into a new course, Mineralogy 12, given in two terms, the work being arranged to permit simultaneous instruction in divisions. The results have been satisfactory, substantial advantages having resulted from the better proportioning of the parts of the course and from the elimination of the long vacation break.

To meet the desires of the Department of Civil Engineering, Mineralogy 5 is now given in one term instead of two, and this year for a similar reason Mineralogy 6 will be given in afternoon hours of the third year instead of in the second year.

The examination of the crystallized material from Texas referred to in the June number resulted in the discovery of three new mineral species, described by Professor Moses in the September number of the *American Journal of Science*, an orthorhombic mercuric oxide, an isometric mercurous oxychloride and a monoclinic mercurous oxychloride. For the isometric mineral Professor Moses has chosen the name eglestonite in honor of the late Professor Thomas Egleston.

Dr. Luquer has completed his description of the decomposed zircon-like mineral, cyrtolite from the pegmatite veins in the "Augengneiss" area at Bedford, N. Y. He has also reëxamined the doubtful substance ramosite, proving that it can not be regarded as a mineral species.

In view of his long service he has been granted leave of absence for six months and will spend it in Europe.

Dr. Rogers has published in the *American Geologist* a description of minerals observed on buried Chinese coins of the seventh century, and has in preparation papers upon crystal habit; gnomonic projection from a graphical standpoint; notes on twinned galena, sphalerite, haidingerite, etc.; a new protractor for the determination of the indices of crystals. In July and August Dr. Rogers was engaged in work for the university geological survey of Kansas, and during the summer collected for the department a suite of lead and zinc minerals from the Joplin district.

It is proposed to establish a Journal Club in the department to meet twice a month for the discussion of new developments in mineralogy, either resulting from the work of the members of the club or as recorded in the current literature.

There is a small but apparently increasing demand for courses in elementary mineralogy for women. The study of nature in the secondary schools appears to be the principal cause of this. Under existing rules only the advanced courses are open to women. To satisfy the demand Professor Moses is giving a University Extension Course on Saturday and the department has offered to start a course at Barnard College.

Specimens have been received for the Egleston Museum of curious pseudomorphs from Utah, diamond in matrix with gold from Brazil. suites of pentlandite and molybdenite from Canada, covellite carrying palladium from Wyoming and the new species hellandite from Norway and an interesting suite of silver, copper, tin and lead, minerals from San José, Bolivia. Several gifts of minerals were also received, including a small collection made by Dr. Minturn Post, of the class of 1827; a number of St. Louis minerals, by Mr. H. A. Wheeler, class of 1880, some sodalites collected by Professor Henry M. Howe.

The equipment for graduate work has not been greatly improved during the year, as most of the departmental appropriation was needed for furniture, apparatus and supplies for the increased number of undergraduates. A gift from Mr. F. A. Schermerhorn, however, was used for the purchase of additional microscopes and of crystal models, the latter including a selected suite of large models made of colored cardboard representing corresponding ideal and distorted forms, and also a suite of small mounted wooden models to be used in the new crystal collection

and representing in each crystal class the general form and those combinations in representative species which are shown in actual crystals. The wooden crystal models cut by the late Professor A. H. Chester in the early days of the School of Mines, and representing abstract forms, have been supplemented by machine-made models of about the same size, representing series of forms of common minerals.

The equipment of the Department has been further improved by the fitting up of a new division Lecture Room (516 S.), with narrow tables and chairs and with twenty duplicate labeled sets of minerals (10,000 specimens), and a lecture set. This room is also equipped with reflection goniometers for student work and with a lantern.

The former lecture room (106 S.) is used at the same hours by the other division as a conference room and contains the student collections, comprising 2,000 labeled hand specimens, 2,000 unlabeled conference specimens, 750 trays of specimens in sets for determination and a new "practice collection" of one thousand unlabeled minerals, 500 large wooden crystal models a series of glass crystal models and natural crystals.

DEPARTMENT OF CIVIL ENGINEERING.

The number of students taking courses in the Department of Civil Engineering continues to increase both in respect to those who are candidates for the degree of civil engineer and those who are taking courses from other departments. This is clearly shown by the statistics of the Summer School of Surveying as well as by the statistics in the registrar's office. The following table shows the attendance at the Summer School each year since 1898:

Year,	1898	1899	1900	1901	1902	1903
Attendance,	52	90	75	119	167	203

In order to accommodate the rapidly increasing needs of the Summer School the University has purchased nearly 600 acres of land at Morris, Conn., including the farm hitherto leased, for permanent quarters for the s hool. Two of the new buildings required have already been constructed and it is hoped that the remainder may be completed before the session of 1904. Each of the new buildings contains nineteen rooms and accommodates fifty-six students. The session of the summer of 1903 was marked with the same degree of efficiency in management and instruction work as heretofore. Under the direction of Professor Lovell the field work of a number of the courses has been extended and made more effective even than hitherto.

More attention has been paid during the past year to the summer memoirs of the third-year students in this department, resulting in more thoroughly technical work and advancing the quality of the memoirs. Two of these papers have been selected for publication in the SCHOOL OF MINES QUARTERLY, one being a description of the proposed sanitary work of Havana, Cuba, and the other a description of the sources of water supply of New York City.

A larger amount of original investigation and research work than usual has been done during the past year, largely in the determination of the elastic properties of concrete and concrete-steel members. The final results of these investigations will add greatly to the knowledge of the elastic

behavior of concrete. Six students of the fourth-year class are also devoting their thesis work to investigations in concrete and concrete steel.

The following changes have occurred in the staff of the department: Mr. A. Black, C.E., instructor, was granted leave of absence for one year from July 1, 1903, to travel and to study the practical operations of sanitary works, subjects in which he is especially interested; Mr. Myron S. Falk, C.E., M.E., formerly tutor in the department, has meanwhile assumed the position of instructor, continuing to give instruction in the same subjects in structural engineering as heretofore; Mr. B. H. Bisbee, C.E., a graduate of Cornell University, has been appointed tutor to take the subjects ordinarily given by Mr. Black, and Mr. W. H. Yates, C.E., a graduate of Columbia University, has been appointed to fill the position of assistant, made vacant by Mr. Wyckoff's resignation.

In spite of the depressed condition of engineering work in general building and railroad operations, all graduates of last year in the Department of Civil Engineering have obtained satisfactory positions without difficulty, and a large number of requests for civil engineering graduates of the university have been made without finding candidates to respond.

During the summer Mr. Falk has been engaged as a member of the State Commission investigating the threatened pollution of New York Bay by the discharge of the proposed trunk sewer from the Passaic Valley.

W. H. B.

DEPARTMENT OF ELECTRICAL ENGINEERING.

Since the issue of the last QUARTERLY the department has secured two Weston laboratory standard instruments by means of which all the working instruments can be readily calibrated. This is a most important addition to the equipment of the department and forms part of the general standardization scheme which has been worked out by the staff.

The Westinghouse Electric & Manufacturing Company has given to the Department a 10 H.P., two-phase induction motor, together with its controller and necessary resistances.

The Crocker-Wheeler Company has presented two motors of 2 H.P. and 1 H.P. of a new type, as well as two sets of field coils. They have also repaired an armature for one of our older type machines. The above apparatus has been secured through the interest and coöperation of two Columbia alumni, Dr. S. S. Wheeler the President and Mr. G. S. Dunn, the engineer of the company.

Gifts from the Municipal Signal Company of Chicago in the nature of police signal boxes, telephone apparatus from the same company, and a complete telephone transmitter from the Fahnestock Transmitter Company have been secured.

An important facility has been added to the electrical laboratories by the introduction of twenty kilowatts of alternating, two-phase current from the mains of the United Electric Light and Power Company. This will enable the laboratories to be operated at any time throughout the year. The direct-current laboratory has been greatly improved by the abandonment of all overhead shafting and driving all dynamos by separate motors. Thus each set of students is entirely independent and can conduct their work much more efficiently and rapidly. This arrangement has required a considerable increase in the equipment, and needs a still further increase which it is hoped will be supplied by the older alumni.

Four interesting and instructive models of modern electric machinery have also been presented by the Crocker-Wheeler Company of Ampere, New Jersey.

The following change has been made in the instructing staff: Mr. F. J. White having resigned as assistant, Mr. T. O'Connor Sloane, Jr., was appointed in his place.

Professor Crocker and Mr. Arendt are revising Volume I. of "Electric Lighting," have written a pamphlet on "Electro-Chemical Industries" for use as a text-book and are preparing a book on the "Essentials of Electrical Engineering" for the engineering profession in general, and as a text-book for the course in electrical engineering given to the mining and civil engineering students of the university.

Professor Crocker and Professor Sever have, during the year, contributed to the text-book material for two correspondence schools.

G. F. S.

DEPARTMENT OF MECHANICAL ENGINEERING.

New Officers. — The following changes have been made: Ralph E. Mayer, appointed Adjunct Professor of Mechanical Drawing; Ira H. Woolson, appointed Adjunct Professor of Mechanical Engineering; Amasa Trowbridge appointed Adjunct Professorof Mechanical Engineering, vice W. L. Cathcart, resigned; Dr. Charles E. Lucke, appointed Instructor in Mechanical Engineering; Abbott M. Cregier, appointed Tutor in Mechanical Engineering.

Professor Trowbridge comes from Lehigh University, where he has conducted similar work to that of which he has charge at Columbia. He is in charge of the courses in naval architecture and marine engineering which are now open. These courses are to be greatly developed and, on account of the excellent facilities so close at hand, should prove very attractive to men desiring to take post-graduate work along these lines.

The power and experimental laboratory under Dr. Lucke's direction, has been developed and improved very greatly during the past year and many facilities for experimental research have been added.

A. T.

DEPARTMENT OF GEOLOGY.

The past year was in many respects the most successful in the history of the department. Four graduate students took the degree of Ph.D. and two others are nearly ready. Mr. George I. Finlay, who has been Assistant in Geology, completed his doctorate and in August was appointed to the chair of Geology in Colorado College, Colorado Springs. Miss Ida H. Ogilvie, who received the Ph.D. degree in January last, has become Lecturer in Geology in Barnard College and is developing a laboratory in the college itself. Douglas Wilson Johnson and Charles Henry Dickson received their degrees at commencement. Dr. Johnson has been called to an instructorship in geology at the Massachusetts Institute of Technology and Dr. Dickson received a similar appointment in the department of chemistry, Queens University, Kingston, Ont.

Mr. H. W. Shimer, who has been for two years Assistant in Paleontology, has accepted the position of instructor in the same subject in the Massachusetts Institute of Technology. Mr. Fred H. Moffit, who was Fellow in Geology last year, was claimed again by the U. S. Geological

Survey in which he holds a commission, and was sent June 1 to Alaska to report on a new placer district. Mr. Moffit plans to return to Columbia in the second term and continue the work for his doctorate.

John D. Irving, '97 Coll., Ph.D. '99, who has been engaged in mining geology on the U. S. Geological Survey since he left Columbia, has been appointed Assistant Professor of Geology in Lehigh University and has taken up his work there this fall. Mr. B. F. Hill, who was Fellow in Geology in 1900, and who has been on the State Survey of Texas since leaving Columbia, has been called to an instructorship in Mineralogy and Petrography in the State University of Texas.

Two summer sessions were held by the department the past season. The first occupied the opening week of June and made headquarters at Larrabee's Point on Lake Champlain, just opposite old Fort Ticonderoga. There were thirty-one in the party with Professors Kemp and Grabau, Mr. Shimer in charge. The area proved very instructive and afforded work for a week upon igneous, sedimentary and metamorphic rocks, and abundant fossils. The second session was held at Golden, Colorado, with the mining students who had been at Aspen. There were twenty-four in the party and again a section embracing igneous, sedimentary and metamorphic rocks was studied. Both at Larrabee's Point and at Golden the structural problems are of exceptional interest and afforded field experience with folds and faults. While in Golden many courtesies were extended by Professor Patton, of the Colorado State School of Mines. Professor Patton accompanied us on several days and opened his lecture room for our use.

After the session was concluded Professor Kemp, who with Dr. Finlay had conducted this work, went to Utah and visited the Tintic district with W. P. Jenney, '69 Mines, and then returned to the East, stopping several days in southwestern Wisconsin to visit the zinc mines there. The latter part of the vacation was passed in work for the U. S. Geological Survey in the eastern foothills of the Adirondacks.

The collections have been enriched by the following acquisitions during the summer: A series of the rare copper ores of the Tintic district, Utah, from W. P. Jenney, to be shared by the departments of Mineralogy and Geology; a superb slab of pyrites from the Kempton Mine, Bingham, Utah, presented by Col. E. H. Wall, of Salt Lake; a series of lead and zinc ores from Hazel Green, Wis., purchased and presented by Professor Kemp.

The department welcomes as Tutor in Geology, Dr. Charles P. Berkey, who comes from the University of Minnesota, where for some years he has occupied a similar position. Dr. Berkey will be in special charge of the geological laboratory and will give courses also in the second term.

Professor Grabau spent nearly four weeks in June and early July in the Schoharie Valley, preparing a geologic map of that classic region for the New York State Survey. Data were gathered for a bulletin similar in scope to ones prepared by him on Niagara Falls and Eighteen Mile Creek. He returned to Columbia on July 6 and took up the summer school work in geology, given for the first time in the regular summer session. Two classes were carried on simultaneously, one in structural, dynamical and physiographic geology and the other in palæontologic and stratigraphic geology, with some attention to the historic development of

the science. Fifteen students were enrolled in the first, and ten in the second course. The laboratories and library were open all the time, and work was carried on under supervision from 9 A. M. to 6 P. M. for five days of each week. On Saturdays excursions were made into the vicinity of New York, for the purpose of studying geology in the field. The field and laboratory work on other days included the making of topographic and geologic models, sections and maps; a compass survey and maps of Morningside Park, with location of ledges, and contouring of certain portions; practice in the determination of dips, strikes and outcrops, and their plotting; making a geologic section across Manhattan and part of the Bronx; observations on waves along the shore; study of mountain folds from Krantz models and field examples; collecting fossils in the field and determination of species in the laboratory; study and drawing of 150 selected types of fossils of the various geologic horizons; and the drawing of a separate geologic map of the United States for each of the greater horizons, *i. e., Cambric, Ordovicic, Siluric,* etc., on an outline ground map. At the conclusion of the courses, a three days' excursion to Kingston and Hudson was made by the classes. The day boat was taken up to Kingston Point, affording opportunity for a study of the banks of the Hudson as seen from the steamer deck. At Kingston the Helderberg series was studied and a section was drawn. Fossils were also collected, and the great unconformity, and the overthrust faults of Kingston hill were worked out. The wonderful exposures of folded strata were studied and sketched. The cement industry was also examined. Two days were spent at Hudson, on Mt. Becraft and Mt. Merino. The formations and their fossils were observed in great detail, and a portion of the folded and faulted district was carefully explored.

At the close of these trips, Professor Grabau went to Alpena, Michigan, where he joined Mr. Edwin Kirk, College '07, who had been collecting Hamilton fossils since early July. Mr. M. I. Goldman, graduate student in Columbia, also joined the party, which completed a stratigraphic and palæontologic survey of the Traverse group of the northern part of the southern peninsula, from Alpena to Petoskey. This work has been carried on for the Michigan geological survey, by Professor Grabau, for the last four years and material enough has now been brought together for a complete monograph on the Traverse fauna of Michigan. This work is now being pushed forward with the assistance of Mr. Kirk in the research laboratory of the department. Miss Rena B. Johnson has been engaged during a part of last spring in making drawings of the fossils for this monograph. By arrangement with the Michigan survey, the types and illustrated specimens are to become the property of the Geological Department of Columbia University, in return for the services given by Professor Grabau in working up the material. This will insure for Columbia the finest collection in the world of this remarkable fauna.

Dr. Carlotta J. Maury (Ph.D. Cornell) has been appointed special assistant in the palæontological laboratory and is actively engaged in arranging collections, particularly the Van Nostrand collection of shells. Mr. Edwin Kirk has also been appointed special laboratory assistant. Much new material has been added to the collections in invertebrate palæontology, by field work, gifts and purchase.

J. F. K.

BOOK REVIEWS.

The Mineral Industry, Its Statistics, Technology and Trade in the United States and other countries to the end of 1902. Vol. XI. *The Engineering and Mining Journal*, New York and London, 1903. Price, $5.00.

We regret to state that this is the final volume of this annual encyclopedia of the mining industry. The eleven volumes of the series will have permanent value to every one interested in the development of the mineral resources of the country, and should be in the library of every mining engineer. It is unfortunate that the lack of financial support by the profession has compelled the publishers to discontinue this valuable work. To a large extent this publication has duplicated the work of the U. S. Geological Survey, though during the past year or so there has been some coöperation between the two publications. The reader of the *Engineering and Mining Journal* will gain by the discontinuance of *Mineral Industry*, as many special articles and valuable monographs will now appear in the *Journal* that formerly were to be seen only in the annual publication. It is to be hoped also that the statistical department of the *Journal*, which was developed under the leadership of Mr. Rothwell, will not be less efficient or less prompt in the future, and that the field so ably filled in the past will not be wholly abandoned.

The present volume, like the three previous ones, is edited by Joseph Struthers, Ph.B. (S. of M., '85), Ph.D., 1895, formerly instructor and of late years lecturer in metallurgy in the School of Mines. Since the publication of this volume Mr. Struthers has accepted the position of editorial assistant to Dr. R. W. Raymond, Secretary of the American Institute of Mining Engineers.

In addition to his duties as editor, Dr. Struthers has written, wholly or in part, the articles on aluminum, alum, antimony, arsenic, asphaltum, barytes, bismuth, borax, bromine, chromium, copper, gems, gold and silver, graphite, lead, magnesite, nickel and cobalt, ocher, phosphate rock, platinum, potassium salts, quicksilver, salt, sodium salts, sulphur and pyrite, zinc and cadmium, many of which articles will also appear under his signature in the Mineral Resources for 1902, to be published by the U. S. Geological Survey.

HENRY FISHER, B S. (S. of Chem., '99), assistant in chemistry and assaying, 1902, was one of the assistants on the editorial staff and contributed articles on ammonium, asbestos, calcium carbide and acetylene, fluorspar, Fuller's earth, mica, besides being joint author with Dr. Struthers of the chapters on barytes, chromium, copper, gems, gold and silver, lead, potassium and sodium salts, zinc and cadmium.

DAVID H. NEWLAND (School of Pure Science, '97) was also on the editorial staff and contributed articles on manganese, petroleum and tin, and notes on copper in Michigan, besides being joint author with Dr. Struthers of the chapters on copper, gold and silver, lead, nickel and cobalt, zinc and cadmium.

Among the other contributors are a number of Columbia graduates. WILLIAM CAMPBELL, Ph.D., 1903, University Fellow 1902–3, Barnard Fellow 1903–4, writes on the "Progress in Metallography in 1902."

ALLAN W. Dow, Ph.B., '88, contributes a paper on "Petroleum and Maltha Products used in the Paving Industry." SAMUEL S. FOWLER, E.M., '84, is responsible for notes on gold, silver, lead and copper mining in British Columbia, where he has been since 1896 as mining engineer for the London and British Columbian Gold Fields, Whitewater Mines, Ltd., Ymir Gold Mines, Ltd., and Enterprise Mines. CHARLES H. FULTON, E.M., '97, Professor of Mining and Metallurgy in the South Dakota School of Mines, gives "A Review of the Cyanide Process in the Year 1902." JAMES FURMAN KEMP, E M., '84, Professor of Geology, Columbia University, has contributed to each of the volumes of Mineral Industry. In this volume he has "A Review of the General Literature of Ore Deposits during 1901 and 1902." JOHN ALEXANDER MATHEWS, A.M. (Chem.), '95, Ph D., '98, University Fellow, 1897, Barnard Fellow, 1900, 1901, 1902, contributes a paper on "Alloy Steels." PARKER C. MCILHINEY, Ph.B. (Chem.), '92, Ph.D., '94, Assistant in Metallurgy, School of Mines, 1894–1900, writes on the "Progress in the Manufacture of White Lead during 1902." CHARLES F. MCKENNA, Ph B., '83, Ph.D., '94, gives a review of "The Cement Industry of the United States during 1902." HEINRICH RIES, Ph.B., '92, Ph.D., '96, University Fellow, 1893–95, Barnard Fellow, 1895–1900, Assistant Professor of Economic Geology at Cornell University, contributes a "Review of the Literature of Clays and Clay Products in 1902." WALTER HARVEY WEED. E.M., '83, U. S. Geologist, furnishes notes on copper, gold and silver mining in Montana.

In addition to the above contributions from graduates of the School of Mines, the volume contains numerous and valuable monographs by well-known engineers, among which may be noted an excellent illustrated article on the "Mechanical Equipment of a Modern Portland Cement Plant," by Frederick H. Lewis. Professor Robert H. Richards contributes a chapter on the "Progress in Gold Mining during 1902," and another on "Recent Progress in Ore Dressing." Professor H. O. Hofman gives a review of "Recent Improvements in Lead Smelting," in which we note several pages on ore sampling. Mr. F. A. Rickard, editor of the *Engineering and Mining Journal*, contributes a valuable monograph on "The Sampling and Estimation of Ore in a Mine," a reprint of the excellent series of articles on this subject which have appeared in the *Engineering and Mining Journal* during the present year.

H. S. M.

Machine Design; Part I., Fastenings. By WILLIAM LEDYARD CATHCART, Mem. Amer. Soc. Mech. Engs., Amer. Soc. Naval Engs., and Soc. Nav. Archs. and Mar. Engs. New York, D. Van Nostrand Co., 1903. Pp. 285. Price —, *net.*

This is a work that especially deserves praise for its thoroughness. While the material in the book is not original the author has collected a vast amount of it concerning the subjects of which he treats.

A great deal of the matter in the chapter on "Shrinkage and Pressure Joints" cannot be found in any other work on machine design, although it is highly important in the designing of some machinery. The same can be said of the part of the work dealing with "Rivets and Riveted Joints." The treatment of these is so exhaustive that the reader is surprised to find that so much can be said of them. The explanations are

also very clear and one is satisfied, on reading the chapters over, that what can be said has been said.

The book is useful to the designer, not alone for telling how any part is made, but because of the reasons it gives for making it so. The young designer, or beginner, will find it especially valuable on account of the vast amount of data it places at his disposal. It is the very data that the beginner needs as it is what he rarely has at his command, until he has had some years of experience. For this reason, if for no other, the book should be in the hands of every designer of machinery.

The work, as published, deals only with "fastenings" from the designer's standpoint, but it contains much else, in the form of descriptive matter, that is both useful and appropriate. It is very much to be hoped that the succeeding parts of the work will appear soon and be as clear and as complete as Part I.

A. T.

Radium and Other Radio-active Substances; Polonium, Actinium, and Thorium, with a Consideration of Phosphorescent and Fluorescent Substances, the Properties and Applications of Selenium and the Treatment of Disease by the Ultra-violet Light. By WILLIAM J. HAMMER, Consulting Electrical Engineer. New York, D. Van Nostrand Company, 1903. 72 pp. $1.00.

The above is the title of a lecture delivered by Mr. Hammer at a meeting of the American Institute of Electrical Engineers and the American Electrochemical Society. It was published in the *Transactions of the American Institute of Electrical Engineers*, and now appears in book form. After a few pages devoted to the principal cases of phosphorescence and fluorescence, 31 pages are given to the radio-active substances, with special attention to radium. After this are described the uses of selenium springing from the influence of light upon its resistance; and the book is concluded with an account of the work of Professor Finsen in the treatment of disease by ultra-violet light. The book contains much interesting information on the subjects enumerated, but the topics treated are diverse, and the method of presentation is much less suitable for a book than for a lecture.

C. W. KANOLT.

Woodbridge School,

FORMERLY

School of Mines Preparatory School.

---

417 Madison Avenue,

Between 48th and 49th Streets, NEW YORK CITY

Twenty-second Year Begins October 1st, 1903.

THE school is well equipped with physical and chemical laboratories, in which the students are required to perform a complete set of experiments illustrative of their recitations in physics and general chemistry. A special laboratory is devoted to qualitative chemical analysis for advanced students.

Five hundred Students of Columbia School of Mines have been instructed in the Woodbridge School. Also a large number have been prepared for Massachusetts Institute of Technology, Stevens Institute, Sheffield Scientific School, Lawrence Scientific School, Troy Polytechnic Institute, Cornell University, and the Classical, Medical, and Law Departments of Harvard, Yale, Columbia and Princeton.

A summer school for students who have failed in June begins August 13th and coaches men for the Fall examinations. All classes are limited to five. College men are coached in Freshman and Sophomore Mathematics and Quantitative Analysis.

An advanced course for older students prepares them to enter the second year class. Last June one of our students received his degree in Electrical Engineering in three years.

Vol. XXV. No. 2. JANUARY, 1904.

THE SCHOOL OF MINES QUARTERLY.

A

JOURNAL OF APPLIED SCIENCE.

BOARD OF EDITORS.

A. J. MOSES, Prof. of Mineralogy.
J. F. KEMP, Prof. of Geology.
R. PEELE, Adj. Prof. of Mining.
R. E. MAYER, Adj. Prof. of Drawing.
E. WALLER, Analytical Chemist.
W. H. FREEDMAN, E. E.,
T. H. HARRINGTON,
Tutor in Drawing

Managing Editor, R. E. MAYER,
Business Manager, T. H. HARRINGTON.

CONTENTS:

Notes on Quantitative Analysis for Mining Engineers, Part II. By Edmund H. Miller..... 119
A Restant Source of Error in Optical Sugar Analysis. By F. G. Wiechmann..... 183
Formulæ for Calculating the Size of Wire Ropes. By Sheldon Smillie. 194
A Method for the Exact Expression of Crystal Habit. By Austin F. Rogers..... 199
Unveiling of a Bronze Tablet in Havemeyer Hall to the Memory of Hamilton Young Castner..... 204

COLUMBIA UNIVERSITY

NEW YORK CITY.

Registered at the New York Post Office as Second Class Matter.

TWO DOLLARS PER YEAR. FIFTY CENTS PER NUMBER.
All Remittances should be made payable to Order of "The School of Mines Quarterly."

Portland Cement

THE LAWRENCE CEMENT CO.

ESTABLISHED 1832.

ERNEST R. ACKERMAN, President

This Company has manufactured and sold during 70 years upwards of **20,000,000** barrels of Cement; marketing the product in all the principal cities of the United States, Canada, West Indies, Philippines and South America.

The old Custom House on Wall Street, built in 1835–37, and the new Custom House on Bowling Green, now under construction, were built with cement sold by this Company.

Used on the Old and on the New Stock Exchange in New York City, on the Brooklyn Bridge and New East River Bridge, and on the new Chamber of Commerce Building.

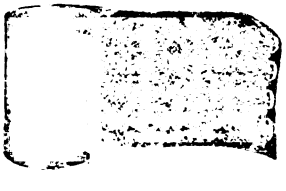
Detailed list of important Government Work Reservoir Dams, Sidewalks, Fortifications, Bridges, Municipal Buildings and Railroad Work where "DRAGON" has been used, furnished on application.

DRAGON PORTLAND CEMENT Stands the Highest Requirements of Architects, Engineers and Builders.

SALES OFFICES:

NEW YORK, No. 1 Broadway. 15th and Market Sts., PHILA.

JENKINS '96 SHEET PACKING



The Perfection of Joint Packing.

Makes joint instantly; does not have to be followed up. Makes joint that will last for years on all pressures of steam, oils, acids, &c. Does not rot, burn, blow or squeeze out.

Received the highest Award **GOLD MEDAL** At the Pan-American Exposition.

All genuine stamped with Trade Mark.

Jenkins Bros., New York, Boston, Philadelphia, Chicago, London.

THE

SCHOOL OF MINES QUARTERLY.

VOL. XXV. JANUARY, 1904. No. .2

CHAPTER VI.

Analysis of Iron Ore.

Under this title the complete analysis of all iron ores might be considered, and then the determination of most of the known elements would be involved as they are occasional constituents of iron ores. However as this is not often required of the chemist, only the determinations of greatest technical importance will be given in detail, namely, iron, silica, sulphur and phosphorus. When only a partial analysis is made, the iron is most easily determined in separate portions, while a larger quantity is taken for the determination of silica, sulphur and phosphorus.

DETERMINATION OF IRON.

By Potassium Dichromate. Penny's Method. — Grind about a gram of the sample in an agate mortar till it feels like flour, from this weigh out two portions of about 0.35 gram each and treat them in small beakers with from one to three c.c. of stannous chloride solution (250 grams per liter), depending on the amount of iron oxide present, and 20 c.c. of hydrochloric acid, 1.1 sp. gr. The beakers should be covered and heated on a hot plate for from ten to fifteen minutes, until the residues are white or until no further solution can be effected. In most cases complete solution of the iron takes place readily if the ore is ground to an impalpable powder but with some ores, particularly magnetites, pyroxene and other insoluble silicates containing iron may be present, which require a fusion with sodium carbonate, etc., to obtain all the iron from the greenish residue.

(*a*) The *residue is white*, the solution may be either colorless or yellow; if it is colorless, an excess of stannous chloride has been added, which must be destroyed by adding potassium permanganate or hydrogen peroxide till the solution becomes yellow, otherwise a black precipitate of mercury would be formed in the next operation. Rinse down the sides of the beaker and the cover and while the solution is still hot add drop by drop a very dilute solution of stannous chloride until the iron is reduced, then dilute to about 50 c.c. and add 10–12 c.c. of a saturated solution of mercuric chloride as already described, and continue the titration as under iron alum.

(*b*) If the *residue is greenish* filter it off and titrate the soluble iron. Fuse the residue with at least six times its weight of potassium and sodium carbonates * in a platinum crucible for half an hour, using a blast lamp if necessary to obtain a clear fusion; dissolve the melt in hydrochloric acid and water and filter out any flocculent silica, washing it with hot water; to the filtrate add an excess of ammonia, filter out the impure ferric hydroxide and wash it twice with hot water; dissolve through the filter by hot dilute hydrochloric acid into a No. 1 beaker, reduce by stannous chloride, add mercuric chloride and titrate as usual by potassium dichromate. Calculate the percentage of iron from the total quantity of dichromate used. It might seem that the hydrochloric acid solution of the fusion could be reduced at once for titration, but there are two objections: first, in the presence of the alkali chlorides, double salts with mercury are formed which are easily reduced, so that a black precipitate of mercury almost invariably results. Second, very often in reducing by stannous chloride the color will become darker instead of lighter. This is due to the formation of platinous chloride from the crucible which gives a very intense color, similar to ferric chloride, but which passes into the filtrate when the iron is precipitated by ammonia.

If exactly fifty times the standard of the solution is taken, twice the number of cubic centimeters used is the percentage of iron without further calculation.

By Potassium Permanganate — Zimmermann-Reinhart Method.† — Treat the ore as for the preceding method up to the point where

* These are mixed in molecular proportions, as this mixture is more easily fusible than either alone.

† Mixer and Dubois, *J. Am. C. S.*, 17, 405.

the silky precipitate of mercurous chloride is obtained, being careful that not more than 15 c.c. of hydrochloric acid 1 : 1 is present. Pour this into 500–600 c.c. of cold water to which 8–10 c.c. of "preventive" solution has been added, and titrate by permanganate as usual, except that the end point is not a pink which lasts for several minutes, but the first tinge of pink which colors the the solution and then fades away in a few seconds.

The "preventive" solution is made by dissolving 160 grams of manganous sulphate in 1750 c.c. of water, then adding 330 c.c. of phosphoric acid 1.7 sp. gr. (syrupy) and 320 c.c. of sulphuric acid 1.82 sp. gr.

This is the neatest and most rapid method for the determination of iron in ores and is very accurate when properly carried out.

We saw that if hydrochloric acid is present in considerable quantity, especially in a hot solution, that titration by permanganate was impossible, as the hydrochloric acid was oxidized with the liberation of chlorine; so the amount of hydrochloric acid present must be small, not over 10 c.c. of concentrated acid in a bulk of 500 to 600 c.c., and the solution cold.

The effect of the "preventive" solution is as follows: The manganous sulphate acts as a sort of carrier of oxygen, it is changed to the manganic condition by any chlorine which may be formed and this in turn is reduced by the ferrous salt back to the manganous condition * and so does away with the bad effect of hydrochloric acid when it is present in not too large amount.

The sulphuric and phosphoric acids give acidity and sharpen the end point by giving a colorless solution at the end due to the preponderance of ferric sulphate and phosphate instead of chloride.

It is important to carry out this method exactly as described, even slight variations are usually disastrous; for example, if the preventive solution is added to the ferrous solution in the small beaker, instead of to the water used for dilution or else after dilution, the silky precipitate is decomposed into mercurous sulphate which may then give mercuric sulphate and mercury and so spoil the determination.

When there is an insoluble residue it is treated as described under Penny's method and the solutions combined or else titrated separately.

---

* Comparable with the action of the oxides of nitrogen in the manufacture of sulphuric acid.

When a complete analysis of an iron ore is made, it may be more convenient to precipitate the iron together with aluminum hydroxide and phosphoric acid in an aliquot part of the solution. This precipitate can be treated by any of the methods given for the ferric alum or for the ore. If titanium should be present it will contaminate the ammonia precipitate and in this case reduction by stannous chloride, sulphurous acid or hydrogen sulphide must be used.

Scheme for the Determination of Silica, Sulphur and Phosphorus in one Portion.

Weigh out 5 grams of the ore ground fine in an agate mortar; heat with 50 c.c. concentrated hydrochloric acid and 7–8 c.c. concentrated nitric acid, to prevent loss of sulphur as hydrogen sulphide, in a beaker for about fifteen minutes; dilute, heat again and filter hot; wash the residue twice with dilute hydrochloric acid. Place the filtrate in a casserole to evaporate on a hot plate or steam bath, with a watch glass over it raised to allow the escape of steam by a glass rod triangle. Burn the paper containing the residue in a platinum crucible, add to it at least six times its weight of mixed carbonates and a small crystal (about 0.2 gram) of sodium nitrate; mix thoroughly with a stout platinum wire or dry glass rod, being careful not to lose any, and fuse for half to three quarters of an hour over a Bunsen burner, then for 10–15 minutes over a blast lamp. Allow the melt to cool and remove it from the crucible in a cake if possible. Place this in a small casserole, then cover it with concentrated hydrochloric acid and regulate the rate of solution by adding water; add the solution of what remains in the crucible dissolved in dilute hydrochloric acid; heat to boiling and boil till everything has dissolved, except possibly some white hydrated silica. There should be no dark or gritty particles left, as these show incomplete decomposition of the ore and require refusion. If the decomposition is complete add this solution to the first solution of the ore (which has been evaporating) and evaporate to dryness; when nearly dry stir so as to form irregular granular masses, which present a large surface and hasten the subsequent dehydration. Place in an air-bath (covered) and heat at 115°–120° C., until no odor of hydrochloric acid is perceptible. If the ore is very siliceous moisten it again with hydrochloric acid and repeat this treatment. Add 15–20 c.c. of concentrated hydro-

chloric acid and heat to dissolve the basic ferric salts; then dilute with water and heat to boiling; filter out the silica which has been rendered insoluble by dehydration and wash alternately with hot dilute hydrochloric acid and cold water, then with water till free from chlorides. Burn the paper containing the silica in a weighed platinum crucible, ignite finally over a blast lamp, cool in a desiccator and weigh. To make sure of the purity of the silica drive it off as silicon fluoride, SiF_4, adding first a few drops of dilute sulphuric acid to hold back any titanic oxide and then adding hydrofluoric acid and warming gently on an asbestos pad, and finally igniting strongly. If any residue is left repeat this treatment till a constant weight is obtained.

If there should be a residue, it is likely to be alumina, titanic oxide or barium sulphate, with possibly traces of iron, and in the present case can be neglected unless barium sulphate or titanic-oxide are present; the first because we are to determine the total sulphur, the second because it may carry down phosphoric acid with it. In either event fuse this residue and leach out the fusion with water (no acid, or barium sulphate would reform) filter and add the filtrate to the main solution. If a fine white precipitate should be formed at this point while the solution is still acid, it will be barium sulphate due to the presence of more than enough barium in the ore to combine with the sulphate and must be filtered out and added to any barium sulphate found as usual.*

Pour the main solution into an excess of ammonia diluted with water in a large beaker, heat, filter and wash first by decantation and then on the filter with hot water till free from chlorides. Evaporate the filtrate down to about 200 c.c., acidify and precipitate the sulphur as barium sulphate using the conditions given under coal analysis.

Treatment of Precipitate containing iron, aluminum and phosphoric acid, also in some cases manganese, titanium, chromium, arsenic, etc. Transfer as much as possible of the precipitate to a No. 3 or 4 beaker and place it under the funnel, pour through the paper hot dilute nitric acid till all the adhering precipitate is dissolved, allowing the solution to run into the beaker containing the bulk of the precipitate, add more nitric acid and heat till the precipitate has dissolved, neutralize with ammonia till the solution is deep red in color but clear, then add nitric acid again till the

* The precipitation may not be complete on account of the acidity of the solution.

red color is just changed to orange, add ten grams of ammonium nitrate and warm the solution to about 60° C., add 100 c.c. of molybdate solution, and allow to stand for half an hour at a temperature of about 45° C. If the operation is to be hastened the precipitation can be done in a flask and shaken for five minutes, wrapped in a towel to prevent cooling, then allowed to stand for another five minutes and the precipitation will be complete, unless the amount of phosphorus present is only 0.01 per cent. or less. Filter and wash with water to which 1 per cent. nitric acid and 10 per cent. ammonium nitrate have been added until the washings give no brown coloration with hydrogen sulphide, showing the complete removal of molybdenum.

The molybdate reagent is made as follows: 100 grams of molybdic anhydride (MoO_3) are mixed with 400 c.c. of distilled water and 80 c.c. of strong ammonia added, the solution of ammonium molybdate is filtered, to remove silica and dust, and poured a little at a time, into a mixture of 300 c.c. of nitric acid 1.42 sp. gr. and 700 c.c. of water; then one c.c. of a ten per cent. solution of sodium phosphate is added to saturate the soluton with the "yellow precipitate" and the reagent is allowed to stand over night. The nitric acid must not be poured into the molybdate as it will give a separation of molybdic acid near the neutral point which is difficult to redissolve. For the same reason the ammonium molybdate should not be added to the nitric acid all at once on account of the heat produced in the neutralization.

We have now, the yellow crystalline ammonium phospho-molybdate, $(NH_4)_3PO_4\ 12MoO_3$, washed free from molybdenum and iron; dissolve this in 100 c.c. of dilute ammonia (1 part 0.9 sp. gr. to 10 of water) nearly neutralize with hydrochloric acid, and add slowly, not faster than 10 c.c. a minute, with stirring an excess of "magnesia mixture." The amount is judged by the quantity of the "yellow precipitate" and should be 1 c.c. for every 10 mgs. of phosphorus pentoxide present. The "magnesia mixture" is made by dissolving 55 grams of magnesium chloride and 70 grams of ammonium chloride in a liter of dilute ammonia, 1 to 10. After stirring briskly add about 8 c.c. of strong ammonia. The precipitate is allowed to stand in the cold for at least four hours filtered, washed with ammonia (1 : 10, containing about 2.5 per cent. NH_3) ignited as already described, heated with the blast lamp and weighed. The percentages of sulphur and phosphorus are reported in an iron ore, not the percentages of SO_3 and P_2O_5.

NOTES, REASONS AND PROPERTIES OF PRECIPITATES.

Some authorities recommend the fusion of the entire five grams to begin with. There are two important objections: First, the cost of the platinum crucible large enough to do it in; second, the introduction of 30–35 grams of alkali chloride into the solution at the start which interferes with clean separations and makes longer washing necessary.

The *dehydration of silica* is an operation of the greatest importance in analytical chemistry and is usually the first step after solution is obtained. If the silica is not removed completely and at once it comes down gradually and contaminates the subsequent precipitates. Then we do not know whether the silica which may contaminate the Mg_2P_2O precipitate is from the ore or from the action of the solutions on the beakers. Ores contain silica as quartz and as silicates of lime, magnesia, iron, etc. Some of these are soluble and others are not, depending on the particular minerals, so that the original solution of the ore may contain silica in solution and the residue insoluble silicates besides silica; when fused with alkali carbonates these give soluble alkali silicates which on acidifying give silicic acids. The evaporation and baking drives the water off these silicic acids, H_2SiO_3, H_4SiO_4, etc., giving when dried at about 100° $SiO_2\frac{1}{2}H_2O$ which is nearly insoluble. This we filter out, but it must be heated by a blast lamp before weighing to drive off the last half molecule of water. It is not to be inferred that one evaporation is sufficient to effect an absolutely complete separation of silica, although it usually suffices for iron ores. Care must be taken not to allow the temperature to go above 120° as there is danger of the reformation of silicates above 140°C., particularly if magnesium is present.

Conditions for Precipitating the Ammonium Phosphomolybdate.— The solution should be slightly acid with nitric acid and contain 20 grams of ammonium nitrate, no tartrates or other organic compounds, and preferably no chlorides or sulphates. The acidity is of great importance; if too acid, the precipitation is slow and often incomplete; if too near the neutral point, the separation from iron is incomplete, and reddish crusts containing iron may form. These are insoluble when the phosphomolybdate is dissolved in ammonia, but may retain phosphorus and must be dissolved in nitric acid and the phosphorus reprecipitated as ammonium phosphomolybdate. In regard to temperature; if too hot (85° or over), or

if allowed to stand for a long time, the precipitate is liable to be contaminated by the separation of molybdic acid; if too cold, say 20° C., the precipitation is slow. The best temperature is about 45° C., for the reasons given, and also on account of arsenic. When this is present and the temperature is high an arsenio-molybdate similar in composition to the phospho-molybdate separates and gives too high results, as it forms with magnesia mixture an insoluble magnesium ammonium arsenate similar to the magnesium ammonium phosphate. Reducing agents and silica should be absent; the latter comes down as hydrated silica, but not as a silicomolybdate.

Solubility of Ammonium Phospho-molybdate. — Readily soluble in ammonia and other alkalies, in alkali phosphates; soluble in hydrochloric acid, strong sulphuric and nitric acids; very slightly soluble in water. Best washed with 1 per cent. nitric acid and 10 per cent. ammonium nitrate, or 1 per cent. sulphuric acid and 10 per cent. ammonium sulphate.

There is no longer any doubt as to the composition of this precipitate when formed under the conditions given, though it may carry down with it somewhat uncertain but relatively small quantities of nitric acid and water of crystallization. When carefully precipitated it may be dried for half an hour at 120° C. and weighed; it then contains 1.63 per cent. of phosphorus.

In dissolving the precipitate very dilute ammonia is used for two reasons: (1) that ammonium molybdate is not very soluble in ammonia, (2) to avoid a great excess of ammonium chloride in the subsequent precipitation.

Magnesium Ammonium Phosphate can be obtained under three different conditions, according to Neubauer.

1. The precipitate is formed in a neutral or ammoniacal solution containing no excess of magnesium salt. Result, the precipitate contains less than the normal amount of magnesium and phosphorus pentoxide is volatilized on ignition. Results low.

2. The precipitate formed is in the presence of an excess of magnesium salt but during its formation ammonia is not present in large excess. Results correct.

3. The precipitate is formed in the presence of an excess of both magnesium and ammonia. Results high.

The other precautions in regard to treating this compound have been given under magnesium sulphate.

There is no advantage in using separate portions for sulphur or phosphorus as they may not be entirely soluble in acids so that when the silica is removed no time is saved. The insoluble phosphorus is supposed to be combined with aluminum and can be rendered soluble by a strong ignition previous to treating with acids.

ADDITIONAL REFERENCES.

MIXER AND DU BOIS. Notes on the Determination of Insoluble Phosphorus in Iron Ores. Trans. Am. I. M. E., Feb., 1897.

BASKERVILLE. On the Analysis of Titaniferous Iron Ores. Journal of the Soc. of Chemical Industry, 19, 419.

POPE. Investigation of the Titaniferous Magnetites, etc. Trans. Am. I. M. E., 29, 372.

WALLER. Analysis of Chrome Ores. J. Soc. Chem. Industry, 15, 436.

CHAPTER VII.

Pig Iron and Steel Analysis.

DETERMINATION OF PHOSPHORUS.

The phosphorus in iron or steel, unlike that in ores, exists as a phosphide, so the first step in the analysis is an oxidizing treatment, solution in nitric acid, with this exception the method given for iron ore can be applied to steel and to pig iron after filtering off the graphite, etc.; but the method is too long for the demands of a metallurgical plant and the "permanganate method" is very generally used. This method has many slight variations but the essential features are always the same. The following description most nearly approaches the methods of W. A. Noyes and of Blair.

Reagents: Nitric acid, 1.18 sp. gr.

Permanganate solution, 12.5 grams per liter.

Ferrous sulphate in fine crystals free from phosphorus (Baker and Adamson).

Ammonia, conc. 0.9 sp. gr.; dilute 0.96 sp. gr.

Molybdate solution as described under iron ore.

Washing solution: Acid ammonium sulphate, made by adding 27.5 c.c. of dilute ammonia (0.96 sp. gr.) and 24 c.c. of concentrated sulphuric acid to water and diluting to one liter.

The standard permanganate already described.

Methods: Weigh out 2 grams of steel or 1–2 grams of pig iron; place in a 500 c.c. flask; add 50 c.c. nitric acid (1.18 sp. gr.) and warm gently till solution is complete, then boil for a minute (with pig irons there will remain a black residue of graphite), add 10 c.c. of the strong permanganate solution and boil till the pink color disappears. The permanganate is added to complete the oxidation of the phosphorus which must be present entirely as an orthophosphate in order to be precipitated as phosphomolybdate. On boiling, the manganese separates from the permanganate as hydrated dioxide. This is cleared up by a reducing agent free from phosphorus, *i. e.*, ferrous sulphate, added in small portions till the solution clears, (with pig iron the graphite remains). At this point, with pig irons, it is best to filter out the graphite, etc., so as to have a clear solution for the precipitation of the phosphomolybdate and

also to save time in the filtering and washing. Cool to about 50° C. and add 8 c.c. * of strong ammonia water for a steel, slightly more for a pig iron, if only a gram is taken. Insert a rubber stopper and shake till the precipitate of ferric hydroxide and phosphate redissolves. Cool or warm the solution until it is as many degrees above or below 60° as the molybdate solution is below or above 27° C. (so that when mixed the temperature will be approximately 45° C.). Add 60 c.c. of the molybdate reagent, insert the stopper, wrap in a towel to prevent cooling and shake vigorously for five minutes, allow to settle for five minutes and filter through a 9 cm. paper. Wash from the top down with the acid ammonium sulphate solution until 5 c.c. give no brown coloration with hydrogen sulphide water (showing the complete absence of molybdenum). Pour over the precipitate 12 c.c. of ammonia (0.96 sp. gr.) diluted to 25 c.c. and allow the solution to run into the precipitation flask. Wash with 100 c.c. water, then add 80 c.c. more water and 10 c.c. of conc. sulphuric acid. Pass this solution through a Jones reductor, with the precautions already described under ferric alum, follow it with 200 c.c. of water and titrate the solution at once in the reductor flask without dilution or delay.

Notes. — This method is entirely satisfactory for steels and, with the modifications given, works well for pig irons; it is not certain whether it is accurate for spiegel or for some special steels containing chromium, tungsten, molybdenum, etc., and should be checked up by the gravimetric method when used on such samples.

With pig iron the amount of ammonia to be used in neutralizing varies and in all cases some judgment must be used and the correct degree of acidity obtained. When only 0.01 per cent. of phosphorus or less is present, the neutralization must be closer and the time allowed for precipitation longer; with pig irons abnormally high in phosphorus (this is shown by the quantity of the yellow precipitate) more molybdate should be added. A difficulty often arises when the ammoniacal solution of the yellow precipitate is acidified — the precipitate separates out again. This can be remedied by more sulphuric acid, or better by redissolving in ammonia and making up to even bulk and taking an aliquot part for acidification and titration. This will avoid the reprecipitation and also using perhaps several hundred cubic centimeters of permanganate.

* This quantity is to be varied so as to obtain a solution but slightly acid as is shown by the color.

The solution as it comes from the reductor should be olive green, the depth of color depending on the quantity of molybdenum. On adding permanganate different colors are formed as the oxidation progresses until finally the solution becomes colorless. It is a pink after this point, which marks the complete reoxidation to MoO_3 and is taken as the end point.

There has been much discussion as to the degree of reduction of the molybdenum after passing through the reductor. Under the conditions which follow, the reduction corresponds to an oxide $Mo_{24}O_{37}$.

There is no evidence of the existence of such an oxide, nor is there a definite stopping point corresponding to this degree of reduction, but under certain conditions the reduction proceeds to this point, viz.: Length of column of 20–30 mesh zinc, 37 cm.; time of passage, about six minutes; temperature, 70°–75° C.; volume, 200 c.c.; acidity, 10 c.c. of concentrated sulphuric acid. The factor for converting the iron standard of the permanganate to the phosphorus standard, based on reduction to $Mo_{24}O_{37}$ is 0.01584; while the factors as determined experimentally * are 0.01579 for unamalgamated and 0.01586 for amalgamated zinc.

The factor 0.01538 corresponds to a complete reduction to Mo_2O_3 and should be used when the molybdenum is reduced as follows: Dissolve the yellow precipitate in ammonia and allow it to run back into the precipitation flask to dissolve what adheres to the sides; the volume is now about 75 c.c.; add 5 grams of pulverized zinc, 100 mesh, and 15 c.c. of conc. sulphuric acid. Close the flask with a rubber stopper provided with a bent tube dipping into a saturated solution of sodium bicarbonate (compare solution of iron wire). Allow to stand for half an hour, then if all action is over and the temperature is about 40° C. it is ready for titration by permanganate. A blank must be run on another portion of 5 grams of the same zinc with the same amounts of ammonia and sulphuric acid and the amounts of permanganate consumed by the iron present deducted from each determination made.

Carbon Determinations.

Steel contains carbon combined with iron, forming different carbides of which cementite, Fe_3C, is one of the most important. Cast iron, in addition to these, contains graphitic carbon. When cast iron

* Miller and Frank, *J. Am. Chem. Soc.*, Vol. XXV., p. 925, 1903

or steel is treated with strong acid the combined carbon is liberated as a hydrocarbon, which is volatile, and so a portion is lost.

When the *total carbon* is to be determined proceed as follows: Weigh out 1 gram of pig-iron; place in a No. 2 beaker; add 100 c.c. of a solution of copper potassium chloride (containing 300 grams per liter) and 7.5 c.c. of concentrated hydrochloric acid. For steel, take 3 grams, 200 c.c. of the double chloride solution and 15 c.c. of concentrated hydrochloric acid. Stir the solution at the ordinary temperature until the iron is dissolved, then heat to about 60° C. and stir till the precipitated copper has gone into solution; allow to settle and filter through ignited asbestos in a small funnel or perforated platinum boat; wash with hot water, dry, and burn the carbon to carbon dioxide in a combustion furnace with oxygen, or in a flask by chromic and sulphuric acids; absorb the carbon dioxide in either potassium or barium hydroxide solution or by soda lime, and from the increased weight calculate the total carbon.

For details see Blair and Cairns' Quantitative Analysis.

The reactions which take place are

$$Fe + CuCl_2 = FeCl_2 + Cu.$$
$$Fe_3C + 3CuCl_2 = 3FeCl_2 + 3Cu + C.$$
$$Cu + CuCl_2 = 2CuCl.$$

The potassium chloride, giving double salts, only hastens the solution.

When the hydrochloric acid exceeds 20 per cent. there is loss of combined carbon.

Graphite is most accurately determined by dissolving 3–5 grams of pig iron in nitric acid 1.2 sp. gr., using 15 c.c. for each gram taken, filtering through ignited asbestos, and then washing with hot water, hot potassium hydroxide solution, 1.1 sp. gr., hot water, dilute hydrochloric acid, alcohol, ether and finally with hot water; then burning to carbon dioxide.

These solutions are used to remove iron salts, silica, hydrocarbons, and the final washing with water is to remove alcohol.

This method is long and for rapid work and approximate results the following may be used. Crobaugh's* method modified. Weigh 2–3 grams of drillings and transfer them to a 125 c.c. platinum dish, add 100 c.c. of nitric acid 1.135 sp. gr. and warm to hasten solution then add about 8 c.c. of 40 per cent. hydrofluoric

**J. Am. Chem. Soc.*, Vol. XVI., p. 104.

acid (B. & A.) and heat for ten minutes. Filter at once on balanced filters, wash with water four times, then twice with hydrochloric acid 1 : 1 or till all iron is removed; then with ammonia 0.96 sp. gr. until the washings are colorless, to remove hydrocarbons, then again with hydrochloric acid and finally with water. Separate the two papers and dry them at 100°–105° C., place one on each pan of the balance and weigh the graphite. Then as a precaution burn them and the graphite in a weighed platinum crucible and deduct any residue found from the weight of graphite. Also examine this residue to see whether any iron compound has resisted solution.

Balanced papers are obtained by taking two from the same package, which have been adjacent and so presumably contain the same amount of moisture, and placing on the two pans of the balance, to determine which is the heavier, then cutting narrow strips off the edges of the heavier till they balance. They are then folded and placed one inside the other and the original solution, as well as all washing solutions passed through both. The assumption is made that as they weighed the same in the beginning and have been treated in the same way throughout, when dried at the same temperature they ought still to weigh the same.

Combined carbon in steel is most rapidly determined by a color comparison as follows:

Weigh out 0.2 gram of the sample and 0.2 gram of a standard steel in which the carbon has been accurately determined by the combustion method, and which is made by the same process and is in the same physical condition, into test-tubes 15 cm. long; add slowly the proper amount of nitric acid 1.2 sp. gr.; for steels containing less than 0.3 per cent. carbon use 3 c.c.; 03.–0.5 per cent. 4 c.c.; 0.5–0.8 per cent. 5 c.c., and so on; place on the top of each test-tube a small glass funnel or marble, put the tubes in a water-bath and heat to boiling, then boil till all carbonaceous material has dissolved, shaking occasionally. This requires 20 to 45 minutes. Pour into graduated tubes and dilute one or the other till the colors match. For example, if the standard steel contained 0.4 per cent. carbon and when diluted to 8 c.c. matched the other steel when diluted to 13 c.c.,— the sample contains 0.65 per cent. carbon.

The entire method depends on having two steels which are almost exactly identical and then treating them exactly alike throughout. Reverse the position of the two tubes when they

appear to match to see whether they still agree in color and so offset any peculiarities in eyesight.

Sulphur Determination.

Sulphur may exist in four different forms in pig iron:

1. That evolved as hydrogen sulphide on treatment with hydrochloric acid.

2. That which is evolved as an organic sulphide $(CH_3)_2S$, etc.; which is neither absorbed by alkaline solutions nor oxidized by bromine to sulphate. It can be decomposed by passing through a red-hot tube mixed with carbon dioxide and then yields hydrogen sulphide.

3. That which is not attacked by hydrochloric acid but is oxidized by nitric acid or aqua regia; perhaps arsenic and titanium sulphides.

4. That which is unacted on by aqua regia and requires a fusion to obtain it in solution.

The methods for determining sulphur are usually classed as evolution or oxidation.

The evolution methods only get the sulphur in (1) but if all the sulphur is present in this condition they are accurate. The amount of sulphur in (2) is exceedingly small and is probably lost by any method in use.

The oxidation methods get (1) and (3) and if the residue is fused (1), (3) and (4).

It has been shown by repeated comparisons that the evolution methods are unreliable in general and can only be used on such material as is known to give up its sulphur by treatment with hydrochloric acid, *i. e.*, steel and pig iron from certain ores.

Oxidation Methods.

*Method of Noyes and Helmer.**—Put 200 c.c. of water and 8 c.c. of bromine (free from sulphur) in a flask and add 5 grams of iron or steel drillings in portions, cooling after each addition. Solution takes place readily, giving ferric bromide and sulphate. When it is complete boil to expel the slight excess of bromine, filter, and wash the residue, set aside the filtrate. To the residue add about 2 grams of sodium carbonate and burn the filter in a platinum crucible, using an alcohol lamp and completing the oxidation by

*J. Am. C. S., 23, 675, 1901.

the addition of a few crystals of potassium nitrate and reigniting. Dissolve the residue in water, filter, acidify the filtrate with hydrochloric acid, add 5 c.c. of barium chloride solution, heat, etc., and weigh the barium sulphate; add three fifths of the weight of barium sulphate found here to that obtained from the filtrate. Place 130 c.c. of 10 per cent. ammonia into a 500-c.c. flask and pour in the filtrate, dilute to the mark and mix thoroughly by pouring into a dry beaker and back; filter through a dry filter. Take 300 c.c. (three fifths) of the strongly alkaline filtrate and evaporate it in a wide beaker to about 100 c.c., taking care that it shall not absorb sulphur from the gas. Then add five to six drops of dilute hydrochloric acid and precipitate the sulphur as barium sulphate in the usual manner. To the barium sulphate so obtained three fifths of that from the residue and calculate the results on three grams of steel.

Notes. — This method is both accurate and rapid. It obtains all but the organic sulphide which may be present. It overcomes the difficulty of washing out the sulphate from the bulky ferric hydroxide from five grams of iron, by taking an aliquot part, and the many troubles which arise when the attempt is made to precipitate barium sulphate in the presence of iron.

In some cases more than eight grams of bromine are required to effect complete solution. The iron should be added slowly and in portions, so as not to heat the solution by a violent reaction and so cause a separation of a basic ferric salt, which is redissolved with difficulty.

The only possible objections to this method are, the error due to the volume of the precipitate when an aliquot part of the filtrate is removed, which is practically nothing with material so low in sulphur, and the possibility of contamination of the barium sulphate from the residue by hydrated silica.

Bamber's Method is equally accurate, but less convenient. Dissolve at least 5 grams of the sample in strong nitric acid; add 2–5 grams of potassium nitrate; evaporate to dryness in a platinum dish and ignite. Boil with water and sodium carbonate, filter and wash with water containing sodium carbonate. Acidulate the filtrate with hydrochloric acid, evaporate to dryness to dehydrate the silica, redissolve in water and a few drops of hydrochloric acid, filter and determine as barium sulphate. For further details see Blair or *Jour. Iron and Steel Inst.*, 1894, p. 319.

Sulphur is also determined * by the precipitation as barium sulphate in the presence of iron, but the method is open to serious objections. On account of the solubility of barium sulphate in hot acid solutions containing ferric chloride the precipitation must be made in a solution only warm and then must be allowed to cool before filtration. Under these conditions the precipitate is not only difficult to filter, but is usually contaminated by iron. The cause of the contamination as given by Kuster and Thiel † is the formation of the insoluble barium salt of a complex ferrisulphuric acid, $Ba(Fe_2S_3O_9)_2$, which loses SO_3 on ignition, so the contaminated barium sulphate may give too low, not too high results, and the purification of the precipitate only increase the inaccuracy. This trouble can be avoided by precipitation in the cold or by pouring the ferric solution into the barium chloride, but it is preferable to remove the iron as given in the methods described.

EVOLUTION METHOD. CAMP'S‡ DESCRIPTION OF THE ELLIOTT METHOD.

Solutions Required.

Iodine. — Weigh into a flask about 18 grams of potassium iodide and 8 grams of iodine; add water and shake till solution is complete, then dilute to about 1.75 liters. This is standardized by steels containing known amounts of sulphur.

Cadmium Chloride. — Dissolve 12 grams of cadmium chloride in about 125 c.c. of water, add 65 c.c. of strong ammonia and filter into a liter bottle; 250 c.c. of water are added and the solution made up to a liter with strong ammonia.

Starch Solution. — Add to half a liter of boiling water in a liter flask, 3–4 grams of pure starch, previously stirred to a thin paste with cold water; this is boiled for ten minutes and, when cold, 3–4 grams of pure zinc chloride are added and the solution diluted to a liter with cold water. The clear solution is siphoned off for use and keeps well.

Method. — Five grams of pig iron or steel are weighed off into a dry half-liter flask, provided with a two-hole rubber stopper, with funnel tube and delivery tube with a rubber-tube connection, which is connected with a glass tube which reaches to the bottom of a test-tube 2.5 cm. wide and 25 cm. deep. In this is placed 10

* Colby's method is given in Cairns, p. 170.

† *Zeits. für anorganische Chemie*, XXII., 424.

‡ Phillips' "Methods of Iron Analysis," p. 41.

c.c. of the ammoniacal cadmium solution, diluted with water so that it fills two thirds of the test-tube. 80 c.c. of hydrochloric acid 1 : 2 (1.07 sp. gr.) are now poured into the flask through the funnel tube and a gentle heat applied till all the iron has dissolved, then heated to boiling until nothing but steam escapes. The apparatus is then disconnected and the delivery tube placed in a No. 4 beaker, and the contents of the test-tube poured in, then the test-tube is rinsed out with 25 c.c. of dilute hydrochloric acid and with water and the rinsings added to the beaker. The volume of the solution should be about 400 c.c., when the cadmium sulphide has dissolved, 5 c.c. of starch solution are added and the standard iodine run in till a permanent blue color is obtained. The iodine can be adjusted to read one hundredth of a per cent. of sulphur for each cubic centimeter when 5 grams are taken for analysis.

The chemistry of the process is as follows: The sulphur is liberated as hydrogen sulphide; this is absorbed by the ammoniacal cadmium solution, giving yellow cadmium sulphide, which is easily dissolved in dilute hydrochloric acid, giving hydrogen sulphide again which remains dissolved in the large volume of water present, 400 c.c. The iodine solution reacts $H_2S + I_2 = 2HI + S$, in a dilute solution. Then the least excess of iodine gives an intense blue with starch which is the end point.

Silicon Determination.

Drown's method or some modification is always used. Treat one gram of borings with 20 c.c. of nitric acid 1.2 sp. gr. in a platinum or porcelain dish or casserole. When all action has ceased add 20 c.c. of sulphuric acid 1 : 1 and evaporate to copious fumes of sulphuric anhydride, allow to cool and dilute carefully with 150 c.c. of water, heat to dissolve ferric sulphate, filter hot and wash first with hydrochloric acid 1 : 1 and then with water till free from iron. Burn off the carbon in a weighed platinum crucible and weigh the SiO_2; check by driving it off with hydrofluoric acid.

Notes.— Nitric acid should be used, not hydrochloric, as there may be a titanium carbide present which is not attacked by hydrochloric acid alone. Modifications are to add both acids at once *i. e.*, nitro-sulphuric acid. This is made by adding 60 c.c. of conc. sulphuric acid to 600 c.c. nitric acid 1.2 sp. gr. 30 c.c. are used for each gram of drillings.

The sulphuric acid takes the water from the silica and so renders it insoluble. This method is more rapid than dehydration by means of heat alone but is limited in its application to those cases where insoluble sulphates are not present. Like the method described under iron ore, traces of silica escape when only one evaporation is made, but the quantity present is so small that a second dehydration is rarely necessary.

Determination of Manganese.

Manganese in steel is usually determined colorimetrically after oxidation to permanganic acid by lead peroxide in a nitric acid solution, but the method proposed by Walters * seems preferable. Weigh 0.2 gram of the steel to be tested and the same quantity of a standard steel of known manganese content into two large test-tubes. Add 10 c.c. nitric acid 1.2 sp. gr. to each and heat them in a water-bath till the nitrous fumes are driven off. Next add 15 c.c. of a solution of silver nitrate containing 1.33 grams to the liter, and then immediately about a gram of moist ammonium persulphate, $(NH_4)_2S_2O_8$, to each; continue heating till the oxidation is complete, then half a minute longer. Remove the tubes, while the oxygen continues to come off, and place them in cold water. When cool compare the colors as described under combined carbon.

Notes.— When the manganese is over 0.75 per cent. use only 0.1 gram of steel. The ammonium persulphate loses its efficiency unless it is kept moist. The method can be applied to pig iron by filtering off the carbon, etc., or can be changed to a volumetric method by titrating the permanganate by a standard arsenite solution as described by Stehman in the *Journal of the American Chemical Society* for December, 1902.

Additional References.

Blair. The Chemical Analysis of Iron.
Phillips. Methods of Iron Analysis.
Lord. Notes on Metallurgical Analysis.
Arnold. Steel Works Analysis.
Brearley and Ibbotson. The Analysis of Steel Works Materials.
Drown. Influence of Silicon on the Determination of Phosphorus in Iron. Trans. Am. I. M. E., June, 1889.
Thackray. A Comparison of Recent Phosphorus Determinations in Steel. Trans. Am. I. M. E., October, 1895.

* Walters, *Chemical News*, Nov. 15, 1901.

SHIMER. Carbon Combustions in a Platinum Crucible. J. Am. Chem. Soc., July, 1899.

DUDLEY AND PEASE. Need of Standard Methods, etc. J. Am. Chem. Soc., September, 1893.

LINDSAY. Colorimetric Method for Sulphur in Pig Iron, etc. School of Mines Quarterly, Vol. 23, p. 24.

SARGENT. Use of Potassium Ferric Chloride for the Solution of Steel in making the Determination of Carbon. J. Am. Chem. Soc., 24, 1076, 1902.

GLADDING. Gravimetric Method of Estimating Phosphoric Acid as Ammonium Phospho-molybdate. J. Am. Chem. Soc., 18, 23.

KILGORE. Titration of Ammonium Phospho-molybdate by Standard Alkali. J. Am. Chem. Soc., 19, 703.

SHERMAN AND HYDE. On the Determination of Phosphoric Acid as Phospho-molybdic Anhydride. J. Am. Chem. Soc., 22, 652.

CHAPTER VIII.

Determination of Manganese in Spiegel and in Manganese Ores.

VOLHARD'S METHOD.

This is based on the following reaction which takes place in a hot dilute neutral solution containing zinc sulphate or nitrate, in which the manganese is present as sulphate or as nitrate : .

$$3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$$

The neutrality is maintained by the excess of zinc oxide present. Many modifications of the original method have been proposed, neutralizing with barium carbonate, sodium bicarbonate, etc., but the only change which is an improvement is Stone's use of nitric acid in the case of spiegels.

The tenth normal permanganate solution may be used again here or if one is to be made up especially, 2 grams per liter is a convenient strength. The manganese standard can be calculated from the iron standard, but it is preferable to standardize against a spiegel of known manganese content.

Manganese Ore. — Treat one gram of the manganese ore, ground extremely fine, in a casserole with 10 c.c. of concentrated hydrochloric acid and if necessary a little nitric acid to ensure the oxidation of the iron present. When pyrolusite, etc., are to be analyzed of course the nitric acid is unnecessary ; heat till complete decomposition is effected, then add 25 c.c. of water and 5 c.c. of concentrated sulphuric acid and evaporate to fumes of sulphuric anhydride; cool, dilute to about 150 c.c. and heat to dissolve the sulphates completely. Examine the insoluble residue to see whether it is completely decomposed ; if not, as would be the case with franklinite, filter; fuse the residue with mixed carbonates, dissolve in hydrchloric acid, evaporate to fumes with sulphuric acid and add the solution, after diluting, to the main portion.

Nearly neutralize the sulphate solution with a saturated solution of crystallized sodium carbonate, transfer to a liter flask and add a cream of zinc oxide (free from manganese) until the precipitate of ferric hydroxide, etc., settles rapidly ; shake after each addition of zinc oxide, so as not to use an unnecessary excess. Allow the

solution to cool and dilute to the mark. Mix thoroughly by pouring into a large beaker and back into the flask; it makes no difference whether any is lost after mixing, as only portions are taken for titration. Either filter through a dry paper and take out portions of either 100 or 200 c.c. each, depending on the richness of the ore, or withdraw such portions by a pipette from the cloudy liquid above the brownish precipitate in the flask.

Place the portions in small casseroles and if 100 c.c. is taken dilute it to about 200 c.c. with water. Heat to boiling, and while hot run in permanganate rapidly 1 c.c. at a time, stirring vigorously with a bent glass rod till a faint pink is seen against the side of the casserole after the precipitated manganese dioxide has settled; then stir hard again to make sure that the color is permanent, for it sometimes stirs out and then more permanganate is required. The first portion is run rapidly to get an idea of the amount required, the others quickly up to within 1 c.c. of the amount used on the first titration; then carefully, a drop at a time, till the faint permanent pink color is obtained. The reason for this is that when the permanganate is run in slowly the dioxide adheres to the sides of the casserole, so that there is no longer a good background for the end point, and also because the solution becomes cold, which renders the reaction less prompt. Several portions can be run from the original gram till satisfactory duplicates are obtained.

With spiegel the method can be made even shorter. Dissolve one gram in about 15 c.c. of nitric acid, 1.2 sp. gr.; boil out fumes, etc., neutralize with sodium carbonate solution, and proceed as described.

Notes. — The original Volhard method required sulphates, but it has been shown that nitrates are permissible but chlorides objectionable. As manganese dioxide is insoluble in nitric acid we cannot use this acid for the solution of all manganese minerals and so Volhard's method is given for ores.

Neutralizing by sodium carbonate is carried on till a reddish color is produced but no precipitate. The zinc oxide is ground up in a porcelain mortar with water and the creamy liquid poured off for use. Lumps of zinc oxide are of no use and by occupying space cause an inaccuracy when we withdraw say one fifth of the solution and consider that it contains the manganese from one fifth of the amount taken. Notwithstanding the error introduced

by the volume of the precipitate and of the zinc oxide it is better not to allow for them as there is another cause of error which this partly compensates. The precipitate formed by the permanganate is not always exactly hydrated MnO_2; it may be very slightly deficient in oxygen. So the best method is to standardize on a similar spiegel or ore in which the manganese has been determined gravimetrically rather than to calculate from the iron standard. Barium carbonate can be used to neutralize but the end point is not as sharp as with zinc oxide. There has been much discussion as to the excess of zinc oxide and the manner of adding it; probably it is best to add but a slight excess in order to precipitate the iron and then after dilution to add more. It is however important to do this the same way each time and exactly as in standardizing.

Chlorate Separation (Hampe).

This depends on the fact that the addition of crystals of potassium or sodium chlorate to a solution of manganese in strong nitric acid precipitates the manganese as dioxide on boiling. If iron is present a small amount precipitates with the MnO_2. Chlorides must be absent or the precipitation is incomplete.

The nitric acid solution is boiled down to expel other acids, etc. 75 c.c. of concentrated nitric acid are added and the solution heated, then 3-4 grams of chlorate, then heated to boiling for ten minutes, allowed to cool somewhat and another portion of chlorate is added, followed by another boiling; after cooling, the dioxide is filtered on asbestos and washed with strong nitric acid, then with water. The oxidizing power of the precipitate can be determined or it can be dissolved and the manganese determined gravimetrically after the removal of the iron. The method is used for spiegel, etc., and is useful for separating small amounts of manganese from large quantities of iron in pig iron, etc. See Ford's and Williams' methods in Blair's "Chemical Analysis of Iron."

Gravimetric Method for Spiegel.

Dissolve one gram of the finely ground sample, for spiegel is brittle and can be pulverized in a harveyized steel mortar, in about 15 c.c. of nitric acid, 1.2 sp. gr., in a small beaker, evaporate to dryness and bake to decompose the hydrocarbons and dehydrate the silica; add 20 c.c. of hydrochloric acid 1 : 1 and heat till the iron is all dissolved; evaporate nearly to dryness to expel nitric acid; take up with water and hydrochloric acid, if necessary

to give a clear solution, and filter out the residue of silica, etc. We now have the iron as ferric chloride, the manganese as manganous chloride in a bulk of about 100 c.c. slightly acid with hydrochloric acid and no nitrates present. To this solution add a solution of crystallized sodium carbonate till a very slight permanent precipitate is formed; dissolve this in a few drops of dilute hydrochloric acid. Transfer the clear deep red solution to a large beaker and dilute with cold water to about 700 c.c.; the solution should remain clear. Add one gram of sodium acetate (3 c.c. of a saturated solution), heat to boiling as quickly as possible and boil for three minutes; slow heating or long boiling gives a slimy precipitate which is hard to filter. Filter through a fluted paper and wash with boiling water. The solution must be filtered hot, as the precipitate is likely to redissolve in the acetic acid present if allowed to cool. Redissolve the precipitate in hot dilute hydrochloric acid and repeat the "basic acetate" precipitation. Combine the filtrates and evaporate them to about 350 c.c.; if any iron separates, filter, dissolve this in hydrochloric acid and make a small basic acetate precipitation to recover any manganese present; combine the filtrates.

Notes on the "Basic Acetate" Separation.

This is one of the oldest and most important separations in analytical chemistry, and depends on the hydrolytic action of boiling water. It serves for the separation of the triad elements, iron, aluminum, chrominum, etc., from the dyad elements manganese, zinc, cobalt, nickel, etc. It is evident therefore that all the iron must be in the ferric condition and the manganese in the manganous, for ferrous iron is not precipitated (dyad), while manganic manganese is. This condition is readily obtained by boiling the solution after oxidation which quickly decomposes the unstable higher chlorides of manganese. The separation may be complete from zinc but has to be repeated to ensure absence of manganese from the precipitate which is likely to retain nickel, cobalt or copper even after several reprecipitations.

Ferric iron is a weak base. We first neutralize nearly all of the free acid (HCl), then add sodium acetate which forms sodium chloride and free acetic acid; the iron is also largely converted to acetate, as is shown by the deep, blood-red color which is formed at this point. The solution is now ready for the hydrolysis. The

rule for dilution is 100 c.c. for every 0.1 gram of iron present, *i. e.*, for 1 gram of spiegel 700–800 c.c. The reagent is in reality boiling water, which, now that we have the ferric iron combined with the weak acid (acetic), reacts, giving a basic acetate of iron and free but largely undissociated acetic acid.

The composition of the precipitate is not uniform as the replacement of $C_2H_3O_2$ groups by hydroxyl goes on as the boiling progresses. It may be $Fe_2(OH)_2(C_2H_3O_2)_4$, $Fe_2(OH)_3(C_2H_3O_2)$, etc. If the boiling is excessive two troubles may arise; the precipitate with many (OH) groups, approaching the hydroxide, is slimy and the acetic acid in solution may reach a concentration where the reverse reaction takes place and the precipitate dissolves. This is most likely to result if the solution is allowed to cool, for then the hydrolytic action is less strong and the reverse action has a chance to progress until equilibrium is again established, and we find iron in the filtrate. The filtrate should be tested for iron by a ferrocyanide, not by a thiocyanate, in this solution containing acetates.

Fresenius gives the dilution already mentioned and the acidity about one per cent. of absolute acetic acid. If too little acetic acid is present the hydrolytic action is too strong and manganese as well as zinc, nickel, cobalt, etc., come down with the iron, alumina, etc. Titanium, if present, is precipitated with the iron, also phosphorus, arsenic and vanadium in combination, as when ammonia is used.

By bearing in mind these principles it is easy to adapt the method to a manganese ore. Here the iron is low, the manganese higher. The chloride solution is neutralized in small volume, the red color will be faint, then diluted somewhat — probably 200 c.c. will be sufficient — then less sodium acetate is added, about half a gram, with perhaps a little acetic acid.

With ferromanganese the procedure is similar, for the manganese is 3–4 times the iron. In the case of an iron ore, when manganese is to be determined, this separation is substituted for the ammonia precipitation, then the manganese is taken out of the filtrate by bromine and the filtrate used for lime and magnesia as will be described under limestone.

The method is of very general application, but must be adapted to the particular analysis. The precipitate is never ignited and weighed, on account of the alkaline salts, etc., if the oxides and phosphates of iron, aluminum, etc., are to be weighed together as

in an iron ore, the basic acetate precipitate is dissolved in hydrochloric acid and reprecipitated by ammonia. It is not advisable to determine sulphur in the filtrate from this method on account of the likelihood of there being sulphur in the reagents.

The description of the gravimetric determination of manganese is taken up in general from this point.

Removal of Nickel and Cobalt.

To the solution in a casserole add ten grams of sodium acetate and a few drops of acetic acid so as to give a solution but faintly acid with acetic; heat to boiling and pass in hydrogen sulphide while hot. This will precipitate the sulphides of nickel, cobalt and copper if present, and manganese ores often contain cobalt; when the solution is saturated with hydrogen sulphide, digest for a time hot, then filter, and wash with hydrogen sulphide water.

Cobalt and nickel are often present and must be removed before we throw down the manganese by bromine, for they also give black higher hydroxides. The conditions for their precipitation as sulphide must be carefully maintained.

Manganous sulphide is soluble in hydrochloric and acetic acids; zinc sulphide is soluble in hydrochloric not in acetic acid.

Nickel and cobalt sulphides, when once formed are insoluble in either hydrochloric or acetic acids, but are prevented from precipitating by either acid in the cold and by hydrochloric or much acetic acid when hot. However when hot and the acetic acid rendered weak by the mass action of the sodium acetate, nickel and cobalt sulphides will precipitate. If they are contaminated by manganous sulphide this can easily be leached out by washing with hydrochloric acid 1.025 sp. gr. saturated by hydrogen sulphide.

The explanation of the strange action of these sulphides is that they exist in two modifications — a soluble and an insoluble — and that on standing or on heating the soluble, which forms first, is converted into the insoluble, which then requires aqua regia for its solution.*

Precipitation of Manganese by Bromine.

The next step is the precipitation of the manganese by bromine. This might seem unnecessary in the case of a spiegel where there are no salts of lime, magnesia, zinc, etc., which give insoluble phos-

* Herz, *Z. für Anorganische Chemie*, 28, 342, 1901.

phates, but there is such an accumulation of sodium salts, etc., that a reprecipitation of the manganous ammonium phosphate is necessary, so that it is a better plan to throw out the manganese as dioxide. Boil out the sulphuretted hydrogen from the filtrate, allow it to cool and add 2–3 c.c. of bromine (not bromine water); heat to expel the excess of bromine and filter; to the filtrate add a few drops of bromine and a little sodium carbonate to bring the solution nearly to the neutral point and heat again to insure complete precipitation of the manganese.

If the solution is too acid the first precipitation may not be complete; if insufficiently acid some manganese may be oxidized to permanganate. When this happens it can easily be reduced by heating with a few drops of alcohol or of sulphurous acid.

The hydrated manganese dioxide is washed with hot water, and then dissolved in a little hot hydrochloric acid 1 : 1 to which a few c.c. of sulphurous acid have been added to cause a ready solution of the dioxide giving manganous chloride (compare addition of stannous chloride in iron ores).

Sometimes in evaporating the filtrate from the basic acetate precipitate manganese dioxide separates out. If this is free from iron it can be filtered and added to the rest.

Precipitation of Manganese as Phosphate.

There can be no doubt that of all the methods so far proposed for the determination of manganese this is the most accurate and satisfactory. To the hydrochloric acid solution add a decided excess, at least five times the calculated quantity of either microcosmic salt, $NaNH_4HPO_4$, dissolved in water or $(NH_4)_2HPO_4$ solution, which is readily prepared by neutralizing phosphoric acid with ammonia till it just turns phenol-phthalein pink; heat, then add ammonia until the precipitate forms but avoid an excess.

The first precipitate is somewhat flocculent and contains $Mn_3(PO_4)_2$; this is heated on the water-bath until it becomes crystalline and settles almost at once when stirred. The $MnNH_4PO_4.H_2O$ so formed is nearly white with a characteristic nacreous luster and is one of the easiest precipitates known to filter and wash. Allow the solution to cool and filter as usual, wash with water or better with a 1 per cent. solution of the precipitant, followed by dilute alcohol; dry separate from the paper; burn the paper, moistened with nitric acid, add the precipitate, ignite strongly and weigh the

manganous pyrophosphate, $Mn_2P_2O_7$. Or else filter on washed asbestos (amphibole not serpentine) in a Gooch crucible and weigh after drying to constant weight at 100–105° C., as $MnNH_4PO_4 H_2O$.

Instead of asbestos, balanced or weighed filter papers may be used.

Notes. — Before applying this method of precipitation the manganese must be separated from all metals except the alkalies. In forming the precipitate there must be a sufficient concentration of NH_4 ions to change the Mn_3PO_4 formed at first to the $MnNH_4PO_4$; this is supplied by the great excess of $(NH_4)_2HPO_4$ or by the precipitant and NH_4Cl when microcosmic salt is used. Serpentine asbestos is soluble in the phosphate solutions and must not be used.

An excess of ammonia turns the precipitate brown. If this happens, dissolve in hydrochloric acid and reprecipitate.

It is best to separate this precipitate from the paper as it occasionally becomes reduced, giving a phosphide which damages the platinum.

Additional References.

Brearley. Estimation of Manganese in Spiegels. Chemical News, 75, 13.

Knorre. Ueber eine neue Methode zur Manganbestimmung. Z. für Angewandte Chemie, 14, 1149.

Hildreth. On the Determination of Manganese in Spiegel. School of Mines Quarterly, 23, 27.

CHAPTER IX.

Determination of Zinc in Ores.

VOLUMETRIC METHOD BY POTASSIUM FERROCYANIDE.

Zinc is precipitated by potassium ferrocyanide in a solution, acid with hydrochloric, according to the reaction: $3ZnCl_2 + 2K_4Fe(CN)_6 = Zn_3K_2Fe_2(CN)_{12} + 6KCl$. The end point is shown by the formation of a brown color when a drop of the solution is placed in contact with a drop of a uranium solution, preferably the nitrate. The brown is caused by the formation of uranium ferrocyanide by the slight excess of potassium ferrocyanide. The method when properly carried out is rapid and yields very satisfactory results; anything which decomposes or oxidizes the ferrocyanide must be absent, *i. e.*, strong acids, chlorine, etc., and also all of the numerous metals which give insoluble or sparingly soluble ferrocyanides. Those most likely to be present in zinc ores are cadmium, copper, iron, manganese, nickel, cobalt, antimony and aluminum.

Solutions. — A standard solution of potassium ferrocyanide, made by dissolving 43.2 grams of the crystallized salt, $K_4Fe(CN)_6.3H_2O$, in cold water and diluting to two liters. One c.c. will be equivalent to about 5 milligrams of zinc; a 5 per cent. solution of uranium nitrate; a solution of ammonium chloride, 10 grams per liter.

Standardizing. — As the end point is not very sensitive, in the presence of hydrochloric acid, it is necessary to deduct from each reading the amount of the solution in excess necessary to give a certain color with the uranium nitrate. Further, as uranium ferrocyanide is soluble in hydrochloric acid, the excess required for a definite color is dependent on the acidity of the solution. Also the composition of the precipitate varies, depending whether the solution is alkaline (NH_4OH) neutral, acid with acetic or acid with hydrochloric; and if the excess of hydrochloric acid is too great, 10 c.c. of concentrated or more, and the solution titrated nearly boiling, there is likely to result a decomposition with the formation of blue precipitates or colors, which spoil the determination.

These considerations make it imperative to decide at once the exact conditions for titration, and then to determine the allowance for the indicator under exactly these conditions.

The following are of the most general application: volume, 200 c.c.; acidity, 6 c.c. of concentrated hydrochloric acid; temperature, 70° C. (about); ammonium chloride present about 10 grams. The ammonium chloride is added as it affects the appearance of the precipitate somewhat and is usually present when the titration is made. It seems to sharpen the end point slightly. These conditions allow for the presence of lead, which is likely to be present from the ore or from the test lead used to remove copper, as 6 c.c. of hydrochloric acid in 200 c.c. completely prevent the precipitation of lead ferrocyanide. More hydrochloric acid makes the allowance for the indicator too large and too uncertain and so impairs the accuracy of the method.

When lead is absent, for ores like franklinite and certain sulphides containing no copper, it is preferable to decrease the acidity to 2 c.c. of concentrated hydrochloric acid and so decrease the allowance for the end point.

To determine the allowance add to a beaker a little less than 200 c.c. of water, 10 grams of ammonium chloride and 6 c.c. of concentrated hydrochloric acid and warm to about 70° C. Place a number of drops of the uranium nitrate solution on a white surface, tile or sized paper. Run in the ferrocyanide solution a drop at a time till, after stirring, the solution in the beaker gives a decided brown with the indicator. The amount used should be less than 0.5 c.c. This value must be determined with care as it is subtracted from the burette reading in every subsequent titration.

Zinc or zinc oxide can be used for standardizing. Really pure zinc is very difficult to obtain as it usually contains iron, arsenic and lead and often other impurities. Zinc oxide can be easily had free from these but should be freshly ignited and allowed to cool in a desiccator to insure the absence of carbonates.

Weigh out two or, better, three portions of ignited zinc oxide each 0.2–0.25 gram; dissolve these in No. 3 beakers in a little strong hydrochloric acid, dilute somewhat, add sodium carbonate till a slight permanent precipitate is formed (or ammonia), dissolve this in a drop or two of dilute hydrochloric acid, add the amount of acid decided on (6 c.c.), and 10 grams of ammonium chloride;

dilute to about 180 c.c., heat to 70° C. and run in the ferrocyanide solution till the indicator is affected as before.

The precipitate is white and settles well when formed in a hot solution containing ammonium chloride, but without considerable experience there is no warning of the end. Here, it is easy to calculate approximately how much will be required and so avoid the tiresome addition of very small quantities; but in general it is better to divide the solution roughly in half, then titrate one half, adding a c.c. at a time, so as to get an idea of the quantity required. If the half took between 18 and 19 c.c. (no color at 18, strong brown at 19) we can add the other half and run up to 35 c.c. with safety and then finish with small additions till the end is reached.

Deduct the allowance for the end point and calculate the standards to the value of 1 c.c. in terms of zinc. They should not show a difference of more than one in the fifth decimal place.

There is a change in the character of the precipitate which seems to coincide with the completion of the reaction given, and so with the ferrocyanide used minus the allowance; this is not certain enough to be used as an end point, but after some experience it will indicate that the end point will be reached in a few tenths of a cubic centimeter.

There are two very different sources of zinc: (1) Zinc blende, sphalerite, with which may be classed the other soluble ores, Smithsonite, calamine, etc., of minor importance. The ore is likely to contain also lead in considerable quantity, always iron and often manganese, copper, cadmium and sometimes antimony. The ores from Wisconsin, Missouri, Virginia and the west all come under this class of soluble ores. (2) Franklinite, which occurs in large quantity in New Jersey. Associated with this mineral, there is also willemite and a zinc spinel. As this ore is not completely decomposed by acids and a large amount of manganese is present a different treatment is required. It is practically free from copper, cadmium, lead and antimony.

Method for Blende and other Soluble Ores. — Weigh out one gram of the finely ground ore and treat it in a casserole or Erlenmeyer flask with 10–15 c.c. of hydrochloric acid, 1 : 1, then add 25 c.c. of strong nitric acid and boil down to about 10 c.c.; add more concentrated nitric acid and sodium or potassium chlorate, a few crystals at a time, boiling between each addition to throw out the manganese, and evaporate off all the liquid, but do not bake. Allow

to cool, and when cold add 7 grams of ammonium chloride, 15 c.c. of ammonia and 25 c.c. of hot water; boil for a few minutes and break up any adhering particles so as to give the excess of ammonia and the ammonium chloride every opportunity of taking the zinc hydroxide into solution. Filter into a flask or beaker and wash the precipitate of ferric hydroxide, etc., well with the ammonium chloride solution, to which a few drops of ammonia have been added.

If there is a bulky precipitate of ferric hydroxide it will undoubtedly carry down zinc with it. Unless the precipitate is very small, dissolve it through the paper by hydrochloric and sulphurous acids into a clean casserole and evaporate down with nitric acid, then treat with chlorate, etc., as before; after washing the second precipitate, combine the two filtrates.

If the filtrate is blue copper is present. If cadmium is also present, neutralize the filtrate, heat and add 3 c.c. of concentrated hydrochloric acid (no more)* and saturate with hydrogen sulphide to precipitate the sulphides of copper and cadmium which may be contaminated by some lead sulphide, filter and wash, and titrate the filtrate as already described. If copper is present but no cadmium, it can be most easily removed by acidifying with 10 c.c. of hydrochloric acid and shaking in a flask with about 30 grams of test lead (20 mesh) till the copper is precipitated, then decanting, washing and titrating as usual.

Aluminum foil is not good for this purpose as when much aluminum is in solution it is partially precipitated and makes the end uncertain. It is also likely to contain iron. The amount of alumina in ordinary ores does not interfere.

Antimony is not likely to be present. It would be removed by the treatment for cadmium.

Notes. — Low† recommends the precipitation of the copper and cadmium as sulphides by hydrogen sulphide in a solution containing 6 c.c. of concentrated hydrochloric acid in a volume of 200 c.c. and the titration of the zinc in the presence of these sulphides as the acidity is sufficient to prevent the formation of much lead sulphide.

It has recently been stated by Waring‡ that cadmium is almost always present in the Missouri zinc ores in quantities from .25 to 2

* The volume is assumed to be about 150 c.c.

† *J. American Chemical Society*, 22, 198.

‡ Paper read before N. Y. Section of the Am. Chem. Soc., Oct. 9, 1903.

per cent. and that it is extremely difficult to effect a satisfactory separation of zinc from cadmium by hydrogen sulphide without retreating the cadmium sulphide to free it from zinc. Also that the presence of cadmium is the cause of a slight discoloration in the ferrocyanide precipitate. In order to avoid the interference due to cadmium, Stone's method of precipitating the cadmium by aluminum foil in a sulphuric acid solution is used. This will, of course, precipitate copper as well, but involves the subsequent precipitation of the zinc as sulphide, to avoid the troubles caused by aluminum salts. The sulphide is dissolved in hydrochloric acid and titrated under the conditions given. Two cubic centimeters of acid will be enough here as there is no lead to be retained in solution and the allowance for the end point will be less.

Although arsenic does not interfere with the titration, it prevents the complete precipitation of iron by ammonia in excess and the excess cannot be boiled out here, for then zinc would be precipitated as $Zn(OH_2).H_2O$. So Low recommends treating the ore with bromine and hydrochloric acid until the arsenic is expelled as bromide.

Method for Franklinite.

Although nearly all the zinc in this ore can be dissolved by a treatment with concentrated hydrochloric acid, it is necessary to fuse the residue to get accurate results. There is also so much manganese and iron present that the chlorate and ammonia separations are not satisfactory.

Fuse two grams of the ore in platinum with about 20 grams of mixed carbonates, dissolve the melt in hydrochloric acid and dehydrate the silica if this is to be determined. Neutralize the filtrate with a saturated solution of sodium carbonate till red, then add pure barium carbonate suspended in water till the iron is precipitated (like the zinc oxide in manganese ore). Make up to an even bulk in a flask, mix and withdraw portions for the determination of manganese and zinc.

A variety of methods can be used here; for rapid results, titrate one portion for manganese by Volhard's method, and in another after adding 1 c.c. of hydrochloric acid 1 : 7 titrate the total manganese and zinc by potassium ferrocyanide. (For details see Stone, *Jour. Am. Chem. Soc.*, 17, 473.) For more accurate work take 500 c.c., equivalent to 1 gram of ore, and precipitate the manganese by

bromine in an acetic acid solution as already described, and in the filtrate, after boiling down to expel acetic and hydrobromic acids, titrate the zinc under the standard conditions. Here the 2 c.c. excess of hydrochloric acid is preferable to the 6 c.c.

Notes on the Barium Carbonate Separation.—Be sure that the barium carbonate used is free from sodium carbonate, which is used to precipitate it. This is done by boiling with a solution of barium chloride for several hours; the barium chloride gives barium carbonate with any sodium carbonate present, while the excess of barium chloride and sodium chloride do no harm.

Have only chlorides present; add the barium carbonate in the cold and withdraw portions or filter without allowing the precipitate to stand long. Under these conditions the following bases are precipitated, according to H. Rose: Al_2O_3, Mn_2O_3, Fe_2O_3, Cr_2O_3, TiO_2, CdO, CuO, As_2O_5, Sb_2O_5, P_2O_5 and others, either rare or not likely to be present.

On long standing, when hot, or when present as nitrate, some zinc is likely to be precipitated. It is well in any case to examine the precipitate for zinc and to reprecipitate if it is found.

In this method the barium carbonate precipitate can be used for the determination of iron volumetrically and the bromine precipitate for manganese either volumetrically or gravimetrically.

Gravimetric Method.

An outline of the plan to be pursued is: (1) Decomposition of the ore. (2) Dehydration of the silica. (3) Removal of the fifth and sixth groups by hydrogen sulphide in weakly acid solution, bearing in mind the ready solubility of lead sulphide. (4) Reoxidation on of the iron. (5) Precipitation of the iron, aluminum, etc., by either basic acetate or barium carbonate. (6) Removal of the manganese by bromine. These operations have been described.

Precipitation of the Zinc as Sulphide.

This is necessary because of the lime and magnesia which are usually present from the gangue of the ore, and which also give insoluble phosphates. Zinc sulphide must be precipitated under carefully regulated conditions so that it will filter rapidly, as it is liable to oxidize to sulphate on standing exposed to the air. The solution should be acid with acetic acid and warm, and contain about 15 grams of ammonium chloride, which favors its separation

in a flocculent form which filters well. Like many other sulphides, it changes its form after precipitation, so it is best to saturate the solution with sulphuretted hydrogen gas and then allow it to stand in a warm place over night with a slow stream of the gas passing through, to prevent oxidation and insure complete precipitation.

Zinc sulphide may be precipitated from an alkaline solution, one barely acid with sulphuric acid, or from solutions of organic acids, citric, formic, etc., and, best by potassium sulphide, K_2S, from an alkaline cyanide solution (separation from nickel).

The sulphide should be washed with hydrogen sulphide water containing ammonium chloride or acetate to prevent its resuming a semi-colloidal condition and running through the filter. It is readily soluble in mineral acids and is likely to be contaminated by other sulphides, particularly those of manganese, nickel, cobalt and iron. There is also danger of zinc sulphide coming down with the lead sulphide in a very weakly acid solution, so that this precipitate should be examined for zinc.

Precipitation as Zinc Ammonium Phosphate.

Dissolve the zinc sulphide in a little dilute hydrochloric or nitric acid into a beaker and boil out the hydrogen sulphide. Nearly neutralize by ammonia; dilute to about 150 c.c. and warm on a water-bath, then add a solution of ammonium phosphate, $(NH_4)_2HPO_4$, containing ten times as much as is required to combine with the zinc. If the precipitate does not form, add ammonia carefully until it separates. Warm on the water-bath until the flocculent precipitate changes completely to the crystalline $ZnNH_4PO_4$; continue heating for fifteen minutes longer, allow to cool and filter. The precipitate may be treated in a variety of ways, but it is best to weigh as $ZnNH_4PO_4$, after drying at 100–105° C., rather than to ignite to pyrophosphate. Filter on paper, wash with a 1 per cent. ammonium phosphate solution, then with dilute alcohol. Dissolve the precipitate through into a weighed platinum dish by dilute nitric acid; evaporate to dryness and weigh as $ZnNH_4PO_4$ after drying at 100–105° (this phosphate has no water of crystallization); or filter on a Gooch crucible, using asbestos, or on balanced filters, as already described. The precipitate is readily soluble in acids or ammonia, and slightly soluble in very large quantities of ammonium salts, especially when hot. Microcosmic salt can be used with ammonium chloride not exceeding 20 grams.

Notes.— The important properties have been given. Any other metal except alkali will cause contamination. On ignition to pyrophosphate, extraordinary care is required to avoid volatilization of zinc. The two points to be observed are a large excess of reagent to get a sufficiently complete precipitation (solubility product large) and sufficient concentration of NH ions to change the flocculent precipitate completely to $ZnNH_4PO_4$. As the $(NH_4)_2HPO_4$ gives both and the excess is easily washed out, it is the preferable reagent.

ADDITIONAL REFERENCES.

LOW. Technical Estimation of Zinc. J. American Chem. Soc., 22, 198, 1900.

MILLER AND HALL. Notes on the Ferrocyanide Titration of Zinc. School of Mines Quarterly, April, 1900.

DAKIN. Determination of Zinc as Phosphate. Chemical News, 82, 101, 1000.

For the electrolytic determination of zinc see Smith's "Electro-Chemical Analysis," 1902.

CHAPTER X.

Limestone Analysis.

The determinations usually required are silica, alumina and ferric oxide (together), lime and magnesia. When a complete analysis is desired carbon dioxide, water, manganese, phosphoric acid, sulphur and organic matter must be determined and sometimes also barium, strontium, chlorine, fluorine, potassium and sodium. Whatever may be required, the most important determinations are the first four, as these indicate the composition with sufficient exactness when the limestone is used as a flux in a blast furnace. For this purpose the determination of sulphur and phosphorus may also be needed.

As this "limestone" analysis, is important also for rocks, clays, cement, water for boilers, etc., it will be given in considerable detail.

SCHEME IN OUTLINE.

Dissolve one gram in 5 c.c. conc. HCl, 1 c.c. conc. HNO_3 and 20 c.c. water with heat in a small casserole, filter.

Residue.	*Filtrate.*
Fuse + $NaKCO_3$ dissolve in HCl and add to filtrate.	Evaporate to dryness and dehydrate in an air-bath, take up with H_2O and HCl, heat and filter.

Residue.	*Filtrate.*		
SiO_2, etc., weigh after igniting with blast lamp. Then drive off SiO_2 by HF. Fuse any residue with $NaKCO_3$ and if Al_2O_3 add to filtrate.	Precipitate twice by ammonia, filter, wash.		
	Ppt. $Fe(OH)_3$, $Al_2(OH)_3$ ± P_2O_5, ignite and weigh.	*Filtrate.*—Precipitate twice by $(NH_4)_2C_2O_4$ in neutral solution.	
		Ppt. CaC_2O_4, wash, ignite and weigh as CaO or $CaSO_4$, or titrate the combined oxalic acid by $KMnO_4$.	*Filtrate.*—Precipitate the Mg as $MgNH_4PO_4$, ignite and weigh as $Mg_2P_2O_7$ dissolve in HCl and reprecipitate.

This scheme is without the detail which is especially important in this analysis, and is given only to show the relation of the different parts of the analysis.

DETERMINATION OF SILICA AND OXIDES OF IRON AND ALUMINUM.

Weigh out exactly one gram of the finely ground sample, transfer it to a small beaker and treat with 20 c.c. of water, 5 c.c. of

concentrated hydrochloric acid and about 1 c.c. of concentrated nitric acid, cover with a watch glass and heat until no further solution takes place. Filter through a very small paper into a small casserole and wash the residue once or twice with water. Place the filtrate and washings on the water or steam-bath to evaporate.

If the limestone contained $CaCO_3$, $MgCO_3$, $FeCO_3$ and SiO_2 only, the residue, after more careful washing, could be ignited and weighed as silica, as in this form it is insoluble in acids. This is sometimes true and saves much time with the analysis, but if there are present silicates of lime, magnesia, etc., these may be insoluble or may give gelatinous silica which dissolves partly, so to ensure accurate results it is necessary to fuse the residue to decompose some silicates and also to evaporate and dehydrate the solution to obtain the soluble silica.

The nitric acid is added to oxidize the iron which may be present as pyrites, FeS_2, or as siderite, $FeCO_3$.

While the filtrate is evaporating, dry and burn the filter containing the residue in a small platinum crucible, then add about six times its weight of mixed carbonates and a crystal of nitrate, the size of a pin head, and fuse for about 15 minutes over a Bunsen buner. The fusion should be perfectly liquid; if it is not, increase the heat or the flux or both until a complete decomposition of the insoluble residue is obtained, bearing in mind the disadvantage of introducing into the analysis large quantities of alkali salts. When cold remove the melt in a cake if possible, dissolve it in hydrochloric acid and water and add this to the solution which is evaporating on the water-bath. Continue the evaporation to dryness, stirring with a glass rod, when the salts begin to crystallize; then transfer to an air-bath and heat at 110° C. until there is no more smell of hydrochloric acid.

If the insoluble residue consisted of silicates of calcium, magnesium or aluminum after fusion there are present $CaCO_3$, $MgCO_3$, $Na_2Al_2O_4$, Na_2SiO_3 and the corresponding potassium salts; on treating with acid these give CaC, $MgCl_2$, $AlCl_3$ and H_2SiO_3, besides NaCl and KCl. After combining the two solutions we have $CaCl_2$, $MgCl_2$, $FeCl_3$, $AlCl_3$, H_2SiO_3, NaCl, KCl, HCl. As the calcium chloride is the predominating salt, the dehydration of the silica will be easy on account of its great affinity for water (compare action of sulphuric acid in Drown's method for silicon), so that in the analysis of an ordinary limestone it is not necessary to repeat the dehydration.

After dehydration treat the mass of salts with hydrochloric acid and water, heat to dissolve the salts of iron and aluminum and filter out the silica, which should be perfectly white. Wash with hot water, being careful to use a wash bottle which gives a very fine stream, so as not to dilute the filtrate to more than 100 c.c. Burn the paper and ignite the silica over the blast-lamp to drive out the last of the water, cool in a desiccator and weigh. Check this by driving off the silica by hydrofluoric and sulphuric acids as already described under iron ore. If there should be a residue it is probably alumina, in any event fuse it with a little mixed carbonate, dissolve the melt in hydrochloric acid and add this to the filtrate from the silica.

To the main filtrate add ammonia in slight excess, and heat to boiling, so that the flocculent precipitate of ferric and aluminum hydroxides collects well. This contains any phosphoric acid present and is probably contaminated by calcium and magnesium hydroxides. Allow to settle, and decant through a filter, leaving all of the precipitate in the bottom of the beaker. Dissolve the precipitate in dilute hydrochloric acid and reprecipitate by ammonia, heat again, filter and wash till free from chlorides by boiling water, avoiding unnecessary dilution of the filtrate. Filter without delay as the alkaline solution will absorb carbon dioxide from the air and so cause contamination due to calcium carbonate. The remedy would be to redissolve in acid, boil out the carbon dioxide and reprecipitate. Burn the paper, etc., moisten the residue with nitric acid and ignite finally by the blast-lamp and weigh the combined oxides of iron and alumina.

Precipitation of Calcium Oxalate.

The filtrate, containing $CaCl_2$, $MgCl_2$, KCl, NaCl, NH_4Cl etc., is made decidedly acid with hydrochloric acid; then enough oxalic acid is added to combine with all the lime and the solution is heated to boiling.

To the boiling solution a few drops of methyl-orange are added and then gradually and with frequent pauses dilute ammonia, till the indicator changes color. The neutralization should take half an hour, then a considerable excess of ammonium oxalate is added and the precipitate allowed to stand for four hours. Next filter and wash with a 1 per cent. solution of ammonium oxalate.* Al-

* Richards, *Z. Anorg. Chemie*, 28, 88.

though if these conditions are carried out very carefully it is possible to obtain a very complete separation of calcium from magnesium by one precipitation, it is safer to redissolve the precipitate in hydrochloric acid, after decanting or filtering, and to reprecipitate as before by neutralizing with ammonia and then adding ammonium oxalate.

The main difficulty in precipitating calcium oxalate is the contamination due to magnesium oxalate. Although this is a perfectly soluble salt it is carried down by the calcium oxalate (adsorption) and not readily removed by washing. An alkaline solution is most favorable to this contamination; so, if to the acid solution we add enough oxalic acid to combine with the lime and then neutralize gradually, the calcium oxalate will be formed in as acid a solution as possible and also in one in which it is somewhat soluble, hence it will be free from magnesium oxalate and also in large crystals which can be easily filtered and washed. The indicator, methyl-orange, turns before an excess of ammonia has been added. If we stopped at this point we would not get complete precipitation of the calcium as there is not yet present any considerable excess of ammonium oxalate, so then an excess of ammonium oxalate is added, which converts the magnesium largely to oxalate, and by the mass action of the C_2O_4 ions the solubility product of calcium oxalate is exceeded, the Ca ions are driven out of solution, and the precipitation of the calcium oxalate is complete. Now that the magnesium is present largely as oxalate, we must not wait too long before filtering, as it has been found that the magnesium oxalate increases on the precipitated calcium oxalate. As the calcium oxalate is very slightly soluble in hot water, it is washed with a solution containing an ion in common, 1 per cent. ammonium oxalate.

If the calcium is to be determined gravimetrically, the ammonium oxalate need not be removed; if a volumetric method (potassium permanganate) is to be used this must be washed out with cold water.

When calcium oxalate is ignited it gives a mixture of carbonate and oxide; this can be heated by a blast-lamp for half an hour or more until constant weight is obtained and the resulting calcium oxide weighed. Great care must be observed to expel all the carbon dioxide and to avoid any reabsorption of this or of water from the air, by cooling in a desiccator and weighing quickly.

After burning the paper, etc., the residue can be converted to sulphate by moistening with dilute sulphuric acid and heating carefully over a Bunsen burner (no blast) till the excess is expelled, then weighing when cold and repeating the treatment until a constant weight is obtained.

When the oxalic acid combined with the calcium is to be titrated by permanganate, proceed as follows: Dissolve the precipitate through the filter with the least possible quantity of hot dilute hydrochloric acid into a large beaker, dilute with warm water, add an excess of concentrated sulphuric acid (5–6 c.c.), ten grams of manganous sulphate, and titrate at about 65° C. Or dissolve through the paper in very dilute sulphuric acid, add more sulphuric acid, warm and titrate.

Besides the properties of calcium oxalate already mentioned, like barium sulphate, when formed in a cold solution, it is very fine and runs through the filter. It is dissolved by mineral acids and is slightly soluble in acetic acid. It should be precipitated in a solution containing no salts other than those of magnesium and the alkalies, as it would be contaminated by barium oxalate, manganous oxalate, etc.

Magnesium Determination.

The filtrate should be about 200 c.c. in volume, and will contain a large amount of ammonium chloride and oxalate. If the amount of magnesium is considerable (dolomite) it can be precipitated in this solution by adding sodium or ammonium phosphate and then an excess of ammonia, etc., as already explained. After igniting and weighing the magnesium pyrophosphate, it is best to dissolve it in dilute hydrochloric acid and to weigh any residue of silica with the crucible. Then subtract this weight instead of the original weight of the crucible, as the ammonia salts are likely to cause contamination of the precipitate by silica from the beakers.

If the amount of magnesia is small, as is usually the case, it will not come down satisfactorily in the presence of the relatively large amounts of ammonia salts. Concentrate the solution as far as possible in a beaker, then transfer to a platinum dish and evaporate to dryness. If the salts crawl up the sides, heat the upper edge of the dish instead of the bottom, best by putting a top on the burner which gives a number of small flames from the sides. Then ignite to drive off the ammonia salts, take up the residue

with dilute hydrochloric acid, filter if necessary (to remove dust and silica) and determine the magnesia as usual.

A very good method of getting rid of ammonium chloride is to add to the very concentrated solution in a casserole (just as the salts are beginning to separate) strong nitric acid and continue the evaporation. The ammonium chloride breaks up and is expelled, probably according to the following reaction:

$$NH_4Cl + HNO_3 = HCl + 2H_2O + N_2O,$$

while the excess of nitric acid helps to decompose the oxalates.

When the oxalates are not destroyed and sodium phosphate is used as a precipitant, the magnesium ammonium phosphate must be washed very thoroughly to remove the sodium oxalate.

Effect of Barium, Manganese or Phosphoric Acid.

If the limestone contained a little barium carbonate and considerable pyrites, barium sulphate would be formed, which would contaminate the silica. After driving off the silica, fuse the residue as usual and, if a precipitate is reformed on acidifying, filter and add only the clear solution to the main filtrate. It might happen that the barium carbonate was in excess of the sulphur, so that only a portion would be precipitated as barium sulphate while some would come down as oxalate and the rest as phosphate. In such a case add dilute sulphuric acid drop by drop before filtering off the silica so as to precipitate all the barium, avoiding much excess, so as not to form calcium sulphate which would contaminate it. Then, after driving off the silica, the barium sulphate can be weighed if pure or fused and reprecipitated.

Should there be *manganese* present it will contaminate the ammonia precipitate unless the precipitation is repeated, and also the calcium oxalate. It is possible to precipitate calcium as oxalate in the presence of iron but not in that of manganese (see slag analysis) so that the manganese must be removed before the precipitate of calcium oxalate. This can be done as follows:

1. After several ammonia precipitations add bromine water and ammonia, warm and filter out the higher hydrated oxide of manganese.

2. Saturate the filtrate, slightly alkaline with ammonia, with hydrogen sulphide and filter out the manganous sulphide.

3. Substitute the basic acetate for the ammonia precipitation and take the manganese out of the filtrate by either bromine or by hydrogen sulphide.

The determination of manganese has been described.

There are cases in which the amount of *phosphoric acid* is more than enough to combine with the iron or iron and aluminum present, so that the ammonia precipitate will also contain calcium as phosphate, which can not be removed by solution and reprecipitation. In such a case add a known amount of iron as ferric chloride, which shall furnish an excess over that required to combine with the phosphoric acid, and precipitate with ammonia as usual. All the lime will be in the filtrate and the ferric oxide from the iron solution added must be subtracted from the weight of the total alumina and ferric oxide.

Applications of the "Limestone" Analysis.

The most important variations when this analysis is to be applied to a *rock* are:

1. Fuse the entire rock with Na_2CO or $NaKCO_3$, because so little will dissolve in acid that the treatment is not advisable.

2. Dehydrate the silica by evaporation on a water-bath twice, or if very high in silica (acid rock), three times. The reason for his is seen when we compare the composition of limestonewith that of rock. Limestone contains perhaps 2–3 per cent. of silica and 45–50 per cent. of lime. Rock, 60 per cent. or even 80 per cent. of silica and a small amount of lime. So that if one hundredth of the silica present escapes the first dehydration, the error is 0.6–0.8 per cent.

3. Always look for manganese in a rock, a green fusion due to manganate when nitrate is added to the mixed carbonates in the fusion, but not always formed without it.

With *clays* the treatment is similar to that given for rocks, but here the percentage of alumina is higher and that of lime and magnesia lower, so that the double dehydration of the silica is necessary, and also the refusion of any residue left after driving off the silica, which will usually be alumina, possibly also titanic oxide. The aluminum and ferric hydroxides must be very carefully precipitated in the presence of ammonium chloride and with but a slight excess of ammonia.

With rock, clay or cement, it is not enough to obtain the combined per cent. of Al_2O_3 and Fe_2O_3; the iron, ferrous or ferric, is also required. This can be done as follows: After igniting and weighing the combined oxides, fuse them for at least forty-five

minutes at a low heat with 8–10 times their weight of potassium bisulphate or potassium pyrosulphate, then at the end add concentrated sulphuric acid to reconvert the potassium sulphate to bisulphate. This changes the iron and aluminum to sulphates and at the same time dehydrates any silica which has previously escaped and has precipitated with the hydroxides. Dissolve the melt in water and sulphuric acid, filter, add the silica to the main portion, reduce the iron in the filtrate by passing it through a reductor and titrate by permanganate.

For cements, which often contain about 22 per cent. of silica and 60 per cent. of lime, two evaporations for silica, and the separate percentages of oxides of iron and aluminum, constitute the important variations from the "limestone" analysis described.

For the best information on rock analysis see Hillebrand, *Bulletin of the U. S. Geological Survey*, No. 176. For cement analysis, report of committee, *J. Society of Chemical Industry*, Vol. XXI., pp. 12–30, 1902, and Hillebrand, *J. American Chem. Soc.*, XXV., 1180, 1903.

This discussion also covers the main portion of slag analysis; the composition of slag varies within wide limits, and there may be present any of the common or rare elements. But bearing in mind that the fifth and sixth groups are taken out after the silica, and the principles of the "limestone" analysis, the special methods given later for typical slags will easily be understood.

Determinations of Carbon Dioxide, Sulphur and Phosphorus.

The other determinations in limestone are made on separate portions.

Carbon dioxide is either found by loss or by direct weight, the methods are given in the text-books.* A rapid method is to fuse about four grams of borax glass ($Na_2B_4O_7$) in a platinum crucible, and when cold weigh; place about one gram of the dried limestone on the top of the borax glass and reweigh. Then fuse with a Bunsen burner till no more gas is given off (no blast), cool and weigh. The loss in weight is carbon dioxide, provided there is no moisture or organic matter present. The method is only approximate, as borax glass is slightly volatile and gives total carbon dioxide, water and organic matter, when the latter are present.

* Cairn's "Quantitative Analysis," pp. 33–37.

The reaction is $Na_2B_4O_7 + CaCO_3 = Na_2B_2O_4 + CaB_2O_4 + CO_2$.

Sulphur.—Unless barium sulphate is present, dissolve five grams of a sample in 15 c.c. concentrated hydrochloric acid and 5 c.c. concentrated nitric acid and 15 c.c. of water in a casserole, evaporate, add more hydrochloric acid and evaporate to dryness to expel the nitric acid and dehydrate the silica; take up with hydrochloric acid and water, boil and filter; neutralize the filtrate with ammonia so that it is just acid with hydrochloric and precipitate the sulphate by barium chloride as usual.

If barium sulphate is present, fuse the residue with mixed carbonates, leach with water, filter out the barium carbonate and add the filtrate to the main solution, dehydrate and precipitate as usual.

Phosphorus.— Dissolve 5 grams in 40 c.c. of dilute nitric acid, evaporate to dryness, take up with nitric acid and water, filter, neutralize the excess of nitric acid by ammonia, and precipitate as ammonium phosphomolybdate, etc., as in iron ore. If the iron and alumina are low, the molybdate precipitation can be omitted. Dissolve 5 grams in hydrochloric acid, evaporate, bake, take up with hydrochloric acid and water, filter; to the filtrate add 2–3 grams of citric acid, to prevent the precipitation of aluminum or ferric hydroxides or calcium phosphate, neutralize with ammonia and precipitate by magnesia mixture direct.

Sulphur and phosphorus are objectionable when the limestone is used as a flux for iron ores.

CHAPTER XI.

The Determination of Copper in Ores and Mattes.

Among the many methods which have been proposed for the determination of copper the electrolytic, iodide and cyanide are of the greatest importance and the thiocyanate and colorimetric methods deserve mention.

As the *method of solution* is the same for all these methods, it will be described first.

For ores, weigh out, depending on the richness, from 1 to 5 grams of the very finely ground sample, so as to obtain about 150 milligrams of copper. Treat this in a covered casserole or Erlenmeyer flask (200 c.c.) with 20 c.c. concentrated nitric acid, 5 c.c. concentrated hydrochloric acid and 5 c.c. concentrated sulphuric acid; heat until all the copper has dissolved and then evaporate to dense white fumes of SO_3 (at this point the blue color will have disappeared, no water being present), allow to cool; dilute with water and heat to dissolve ferric sulphate, etc.; filter out the residue, which consists of silica, silicates and the insoluble sulphates of lead, barium, etc., wash this residue with hot water thoroughly, taking care to avoid unnecessary dilution.

This treatment will dissolve the copper in all ordinary ores, but if it is present as silicate (chrysocolla or slags) the residue should be fused with mixed carbonates to ensure complete decomposition.

For mattes, use 0.25–0.5 gram and half the quantities of nitric and hydrochloric acids and about 4 c.c. of sulphuric acid. Alloys such as brass, german silver, etc., can be treated in the same way when it is desired to separate out the lead as sulphate; or dissolved in nitric acid alone, depending on the methods to be used for the subsequent separations. With bronze nitric acid alone is used followed by long boiling in a very dilute solution, so as to separate out the tin as completely as possible, as metastannic acid. This often contains copper which is separated from tin by digesting the residue on a water-bath with potassium sulphide (not ammonium sulphide). This also applies to brass and german silver when they contain tin.

Electrolytic Method.

The sulphuric acid solution containing $CuSO_4$, $Fe_2(SO_4)_3$, etc., besides the possible impurities, arsenic, antimony, bismuth, can be electrolyzed directly, provided there is not too great an excess of sulphuric acid present. 2–3 c.c. of concentrated acid in a volume of about 100 c.c. is a suitable quantity; if this is exceeded a portion can be neutralized by ammonia. If the copper is from a chalcopyrite there will be a considerable quantity of ferric sulphate present, and the separation of copper succeeds best under the conditions given. It is impracticable to precipitate the iron by ammonia before electrolysis as the ferric hydroxide always carries down copper. If difficulty is encountered in depositing the last traces of copper, the solution after electrolysis can be made alkaline by ammonia and when there are only traces of copper present, the amount held by the precipitate can be neglected. In the filtrate the copper can be determined colorimetrically or the solution made acid again by sulphuric acid and the electrolysis continued.

The colorimetric estimation consists in comparing the shade of blue in the ammoniacal solution with the color of standards made up containing known amounts of copper in the same volume and having the same excess of ammonia and at the same temperature. For the details of this method see Heath, *J. Am. Chem. Soc.*, Vol. 19, p. 24, 1897, and Smith, *Trans. American Institute Mining Engineers*, 30, 851, 1901. When arsenic and antimony are present in large quantities, the method described, or any other electrolytic method, fails to give accurate results, as some of these impurities are deposited with the copper. This may be remedied by roasting the material before dissolving (after weighing), or by repeated evaporations with bromine, or by heating the precipitated sulphides with a solution of sodium or potassium sulphide, filtering and then dissolving the copper sulphide in nitric acid.

When the arsenic and antimony are present only in exceedingly small quantities the presence of nitric acid prevents or retards their deposition, so that the best conditions for the electrolysis of a copper matte are, as regards acidity, 2–3 c.c. of sulphuric acid 1.84 sp. gr. and 2 c.c. nitric acid 1.42 sp. gr. in a volume of about 150 c.c.

Bismuth is the most troublesome metal in connection with all the methods for copper; it is not removed by roasting, and although not easily precipitated completely by the current, it al-

ways contaminates the copper when present, often without causing any perceptible discoloration of the deposit. If present, dissolve the deposited copper in nitric acid, add ammonia in excess, then ammonium carbonate, dilute to 150 c.c. and boil. The bismuth is precipitated as a basic carbonate, contaminated by copper; by resolution in nitric acid and reprecipitation it can be obtained pure; then washed, ignited and weighed as Bi_2O_3. The calculated weight of bismuth is deducted from the weight of the deposit.

When the bismuth is present in large amount, or when it is also to be determined, the method described by Riederer, *J. Am. Chem. Soc.*, Vol. XXV., p. 919, 1903, can be employed.

The special apparatus required for the determination of copper consists of platinum electrodes and a suitable stand.

The anode is usually made of a stout platinum wire, bent into a spiral when a cylindrical cathode is used or coiled into a disc when a platinum dish is used. The cylindrical cathode is most convenient when many determinations are made at the same time; it should be open at the side so as to allow the circulation of the electrolyte. Both electrodes should be thoroughly clean, free from deposited metal, grease or dust. This is obtained by treatment with nitric acid or with alcohol and then drying above the flame of a burner.

The cathode is then weighed and connected with the negative pole of the battery or source of electricity, while the anode is connected with the positive pole. With cylindrical electrodes the copper solution is placed in a small but tall beaker and the cathode adjusted so that about half an inch is out of the liquid, and the beaker covered by a divided watch glass or two pieces of mica to keep out dust and prevent loss by spattering. With a dish, a watch glass with a hole in the center for the anode to pass through, is used as a cover.

The area of the cathode should be about ten square inches and the current 1.5–2 volts and 0.1–0.2 ampere. It is turned on and the copper allowed to deposit for from twelve to fifteen hours, then if the electrolyte is colorless the cathode is lowered about one fourth inch so as to expose a fresh surface of platinum for deposition and the electrolysis is continued for an hour longer. When no more copper is deposited, a few c.c. of the solution are withdrawn by a pipette and tested with freshly prepared hydrogen sulphide water on a white surface. This test is much more delicate than the blue color with ammonia.

As there is nitric acid present the cathode must be removed while the current is still passing, otherwise the nitric acid would immediately begin to redissolve copper. This can be done by siphoning out the contents of the dish and at the same time adding water, until the solution is too dilute to attack the deposit, or if the electrolysis is done in a beaker, the block beneath it can be removed and a beaker of water substituted, then the cathode is allowed to drop into the water.

The deposited copper must be dried without oxidation; so it is next rinsed off with alcohol to displace the water, then, when great precautions are required, with ether and is dried at a very gentle heat—such as can easily be borne by the hand—so as not to oxidize the deposit. When cold it is allowed to stand in the balance room for about ten minutes and then weighed.

For the electrolytic assay as applied to refined copper, see Heath, *Trans. A. I. M. E.*, July, 1899.

The behavior of the elements likely to be present, under the conditions given is briefly as follows: Iron does not interfere unless insufficient sulphuric acid is present. Then the nitric acid becomes reduced to ammonia, which precipitates ferric hydroxide. In the directions given, the amount of sulphuric acid is sufficient to neutralize all the ammonia formed, even if the nitric acid is completely reduced.

Nickel and cobalt do not interfere in a strongly acid solution. They are, however, deposited in an ammoniacal solution, if the current is strong. Zinc requires the presence of a strong acid to prevent its precipitation, *i. e.*, nitric; it may be deposited in an extremely weak sulphuric acid solution or readily from solutions of organic acids, like acetic, citric, lactic, etc. So that if the electrolysis is prolonged and the free nitric acid reduced zinc may be deposited. Manganese does not deposit as metal, but goes to the anode as peroxide; it is sometimes oxidized higher to permanganic acid which gives a color to the solution about the anode. Lead in traces escapes precipitation as sulphate and appears on the anode as PbO_2. Bismuth contaminates the copper and also goes to the anode as peroxide. Arsenic and antimony are liable to contaminate the copper as explained.

Silver will be removed as chloride, unless the digestion with concentrated sulphuric acid is very long, then it is partly changed to sulphate. If present, it will deposit completely with the copper;

but is easily removed by a drop of a chloride. Gold, platinum, etc., would be deposited, but are not likely to be present in sufficient quantity to influence the results.

In general salts are objectionable, although in some cases they are added. For example, Classen precipitates copper and other metals from a solution containing large amounts of ammonium oxalate. Hydrochloric acid and chlorides should be absent, as they cause the deposit to be spongy.

For a detailed discussion of the quantitative deposition of metals by electrolysis see "Electrochemical Analysis," by Prof. E. F. Smith, 1902.

It is of the greatest importance that a dense firmly adherent deposit be obtained, free from impurities; aside from the chemical conditions, the character of the current has much influence on that of the deposit.

To describe the current we must know the voltage and amperage; the latter is often given as current density, that is, the number of amperes per 100 sq. cm. of cathode area. ND.100 = 0.2 means 0.2 amperes for each 100 sq. cm. of the submerged area of the cathode on which metal is deposited.

The amperes determine the rate of deposit, according to Faraday's law, but in quantitative analysis the character is of greater importance than the rate, so for copper a low-current density is used, 0.1–0.15 ampere, because a stronger current (except in special cases) is liable to give a dark, spongy and non-adherent deposit, which is difficult to dry without oxidation, and to weigh without loss.

The voltage should also be low enough to overcome the counter-electromotive force of the solution and its resistance; for copper about 1.5 volts, but not a high voltage, as it tends to increase the impurity of the deposit. The best current for electrolytic work can be obtained from storage batteries, or primary batteries; but as the lighting circuits are more convenient, they may be used by inserting a suitable resistance.

The counter-electromotive force necessary to deposit a metal can be calculated from the heat of formation of the molecule, and the results so obtained agree well with those found by experiment. But the question may well be asked, if salts, such as copper sulphate, are already ionized in solution, why is all this energy required to pull the copper sulphate apart? The answer is found in

Nernst's solution-tension theory. This is, briefly, that each metal has a certain power of forcing its atoms into solution as ions; just as a liquid continues to evaporate at its surface till the pressure of the vapor becomes equal to the vapor-tension of the liquid, so the metal sends ions into solution till the osmotic pressure of these ions becomes equal to the solution-tension of the metal. Therefore, in order to separate out the copper ions in the form of metallic copper, a certain electrical pressure or intensity of current is required, so that the sum of this and the osmotic pressure shall exceed the solution tension.

These differences in solution tension for different ions can be found in the books on physical chemistry, and while the results agree well with the old method of calculating counter-electromotive force, the modern method is more accurate, as it considers the variation of voltage with dilution.

There is therefore a minimum voltage below which any given metal will not be deposited, so that theoretically, if all metals gave soluble sulphates or nitrates, we could apply just voltage enough to overcome the solution tension of the lowest in the series and when that metal was completely deposited, the current would cease to pass; then by raising the current to just above the intensity required for the next metal, that could be deposited and so on. This is evidently not possible in all cases, but it is in some. If there are present in solution copper and silver as nitrates and a current of one volt is passed, only silver is thrown out. If the sulphates of copper and zinc are in solution (containing but a trace of free sulphuric acid) we can by keeping the current between 1.5 and 2 volts deposit only copper; while by raising the voltage so as to exceed the solution tension of the zinc, we can deposit brass and by varying the voltage, vary the percentage composition of the alloy.

To return to the copper, we can prevent some metals from depositing by the character of the solution, addition of acid, etc., others will not come down in an aqueous solution at all, others can be prevented from contaminating the copper by regulating the voltage so that the counter-electromotive force of copper is just exceeded. Practically it is often easier to remove the interfering element than to regulate the voltage, and then, when there is no metal present which will come down at a higher voltage, we need only adjust the amperage or current density so as to get a deposit suitable for weighing.

Additional References.

"The Elements of Electrochemistry," by LeBlanc, translated by W. R. Whitney for the theory, and "Quantitative Chemical Analysis by Electrolysis" by Classen for other methods.

Iodide Method.

In an acetic acid solution, potassium iodide precipitates cuprous iodide, with the liberation of iodine, according to the reaction:

$$2Cu(C_2H_3O_2)_2 + 4KI = Cu_2I_2 + I_2 + 4KC_2H_3O_2,$$

or one atom of iodine is liberated for each atom of copper present in the cupric condition.

The liberated iodine can be titrated by a standard solution of sodium thiosulphate, using starch solution as indicator, according to the reaction:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

Here copper acts as an oxidizing agent, liberating iodine, which is measured, and so the copper is determined; a method of indirect titration. It is evidently essential to the success of this method that there should not be present any other oxidizing or reducing agents, for the first would liberate iodine and cause too high results; the latter would be oxidized by the iodine liberated and cause too low results.

The *indicator* is a solution of starch which gives an intense blue color to the solution in the presence of free iodine. The end point is the discharge of this blue color and is extremely delicate when the proper conditions have been observed. The starch solution is made by mixing about one gram of pure starch to a thin paste with cold water and then pouring it into about 200 c.c. of boiling water and boiling for several minutes. It should be allowed to cool and only the clear solution used. This solution does not keep well; moulds grow in it which split up the starch giving dextrins and other carbohydrates, some of which give reddish colors with iodine. To guard against this a preservative such as zinc chloride or carbon bisulphide may be added.

A *standard solution of sodium thiosulphate* is made by dissolving 19.6 grams of the crystallized salt, $Na_2S_2O_3 \cdot 5H_2O$, in water and diluting to one liter. Each c.c. will be equivalent to about 5 milligrams of copper. Standardize as follows: Weigh out two or three

portions of pure bright copper foil of 100–150 milligrams each, taking different weights, as this ensures a really independent determination and saves the time required to weigh out an exact amount. Dissolve the copper in small beakers in about 10 c.c. or less of nitric acid 1.2 sp. gr., evaporate until all red fumes and all excess of nitric acid are expelled, best on a steam bath; redissolve the copper nitrate in a little water, add a few drops of sodium hydroxide, which should give a slight precipitate of cupric hydroxide, dissolve this in a few c.c. of acetic acid, allow to cool and dilute with cold water to about 50 c.c.

Next add three grams of potassium iodide crystals (or in solution), stirring until they have dissolved. The solution now contains a precipitate of almost white cuprous iodide and is colored brown by the liberated iodine. Run in the sodium thiosulphate solution from a burette until the brown color is very faint, a light straw color, then add about 5 c.c. of the clear starch solution and continue the titration until the blue is discharged. Near the end the sodium thiosulphate must be run in drop by drop and the solution stirred thoroughly. Titrate the other portions and calculate the value of the solution in terms of copper. The standards should not differ by more than one in the fifth decimal place (third significant figure).

The blue color will return after a time due to oxidation by the air. If the solution remains colorless for two minutes the end has been reached and the titration is satisfactory. If the blue reappears almost immediately there is probably some oxidizing agent present and if this continues after the addition of a couple more drops of thiosulphate solution the determination is useless.

After the potassium iodide has been added the solution must be kept cold to avoid loss of iodine and titrated without delay to avoid oxidation by the air. As large amounts of sodium acetate interfere with the end point, by causing a return of the blue color, care should be taken to add only a few drops of sodium hydroxide solution (not carbonate) in neutralizing the nitric acid.

Assay. — To the sulphate solution of the ore or matte add two pieces of sheet aluminum, one sixteenth inch thick and one and one half inches square, whose corners are bent so that the two pieces only touch at the points and so present a large surface, then about 5 c.c. of strong sulphuric acid. Heat to boiling, covered to prevent spattering, until all the copper is precipitated. Pour

the solution and that portion of the copper which does not adhere to the aluminum foil into a clean beaker and allow the copper to settle; then decant through a filter, wash the aluminum foil coated with copper, with water and the copper in the second beaker, pour the washings through the same filter; remove the vessel containing the filtrate and washings and substitute the other beaker containing the non-adherent copper; to the beaker containing the aluminum foil add 5–6 c.c. of nitric acid 1.2 sp. gr. and warm till all the copper has dissolved, then pour the acid copper nitrate solution through the filter into the beaker below, which contains the rest of the copper and heat till all the copper has dissolved.

If the precipitated copper is red in color and evidently pure, the washings of the beakers and filter can be added at once and the excess of nitric acid expelled and the copper titrated exactly as in standardizing. If the copper is dark, before diluting with the washings add half a gram of potassium or sodium chlorate and boil to oxidize any arsenic which may be deposited with the copper, then add the washings and evaporate as usual. When antimony is present it will be oxidized by the nitric acid and be almost all filtered out; the traces which dissolve must be oxidized like the arsenic. It is of the utmost importance that all the chlorate is decomposed and the chlorine and oxides of chlorine boiled out, as these would liberate iodine later on.

Bismuth will be deposited with the copper by the aluminum, it will dissolve in nitric acid and unless thrown out as a basic salt when the copper nitrate is dissolved in water, will precipitate as a brown iodide, BiI_3. As this is not attended by any liberation of iodine it will not affect the results, but as this iodide is somewhat soluble in potassium iodide a brown-colored solution is produced, which may look like liberated iodine, and so too much thiosulphate solution may be run in before the starch solution is added.

In titrating some ores the end point may not be exactly the same as with pure copper, due to impurities, such as bismuth, lead, etc., which give a greenish solution after the starch is added, so that the change is not from blue to white, but from a dirty green to a yellowish white.

The amount of potassium iodide has been given as three grams; this quantity is required for the reaction and the excess necessary to hold the liberated iodine in solution. More does no harm, but as the reagent is expensive, it should be used sparingly. The end

point is so sharp that slight variations of the volume or of the amount of copper present have no effect. Ferric salts cannot be present, as they liberate iodine; in the method described they are reduced to the ferrous condition when the copper is precipitated by aluminum and are thrown away in the filtrate. If sodium carbonate is used instead of hydroxide in neutralizing the copper nitrate solution some copper remains in solution as bicarbonate. Then, when the potassium iodide is added, iodine and carbon dioxide are liberated together, and some iodine is lost by being carried out with the carbon dioxide.

It has been proposed recently by Low to neutralize here with ammonia and then to acidify by acetic acid as described: also to oxidize any arsenic or antimony present to the pentad condition by bromine instead of chlorate. For further information on this method see: Low, *J. Am. Chem. Soc.*, 18, 458 and 24, 1082, 1902. Beringer's "Assaying," p. 160.

Potassium Cyanide Method.

This method is very largely used, as it is more rapid and less expensive than the iodide method. It depends on the conversion of the intensely blue $Cu(NH_3)_4$ ion into a colorless $Cu(CN)_2$ ion, or practically the measurement of the amount of potassium cyanide solution necessary to decolorize the ammoniacal solution of copper nitrate or sulphate.

The reaction for the sulphate is given by Treadwell as follows:

$$2Cu(NH_3)_4SO_4, H_2O + 4KCN = 2Cu(CN)_2 + 8NH_3 + 2K_2SO_4,$$

then the $2Cu(CN)_2$ breaks up, giving $Cu_2(CN$ and $(CN)_2$, and, if sufficient potassium cyanide is present, forms $K_4Cu_2(CN)_6$, while the $(CN)_2$ reacts on the excess of ammonia, like Cl on KOH, giving NH CN and NH_4CNO. So the complete reaction is,

$$2Cu(NH_3)_4\ SO_4,H_2O + 8KCN = K_4Cu(CN)_6 + NH_4CN$$
$$+ NH_4CNO + 6NH_3 + 2K_2SO_4.$$

This is not advanced as a perfect explanation of what takes place, but to show how complex the simplest form of the reaction is. Then if we begin to consider the influence of other salts present and the easy conversion of ammonium cyanate into urea, a large field of possible organic compounds is opened; so it is evi-

dent that the reaction must be carried out under identical conditions in order to obtain accurate results. The following facts also emphasize this:

1. Increase of temperature decreases the intensity of the blue color.

2. A large excess of free ammonia tends to vary the color and give low results.

3. Ammonium sulphate gives low results.

4. Hydroxides, bicarbonates, sulphites and nitrites affect the results.

5. Salts of silver, zinc, nickel, etc., which react with potassium cyanide must be absent.

6. Ferric or manganese hydroxides should not be present, as they hold copper and mar the end point.

The titration must therefore be made in the absence of iron, manganese, zinc, nickel or silver salts, best without ammonia salts, at the same temperature (the lower the sharper the end point), with the same excess of ammonia, with the same volume at the end, and with approximately the same amount of copper present.

Make up a solution containing 22 grams of pure potassium cyanide per liter. Weigh out two or three portions of pure copper about 150 milligrams each; dissolve them in nitric acid, in a beaker capable of holding 200 c.c. easily, with a mark at 150 c.c.; boil out the oxides of nitrogen; dilute with cold water to about 80 c.c.; neutralize with dilute caustic soda solution till a faint permanent precipitate forms; then add 6 c.c. of strong ammonia (0.9 sp. gr.) and run in the potassium cyanide solution till the blue color is very faint; dilute to the mark (150 c.c.) and continue the titration until the solution is colorless.

To apply the method to ores, etc., follow the directions given for the iodide method until the copper is precipitated on aluminum foil, dissolve this in nitric acid and proceed as in standardizing.

The method is very accurate after a little experience with the end point, and its most important feature is the necessity of absolute uniformity in the conditions of titration. Should great rapidity be required at the expense of accuracy, the ore can be dissolved in nitric acid, an excess of ammonia added, then titrated to a faint blue, the residue ferric hydroxide, etc., filtered out, and the titration finished on the clear filtrate.

The cyanide solution keeps best in the dark, but as it is constantly losing hydrocyanic acid it requires frequent standardizing.

For further information see: Beringer's "Assaying," p. 154, and H. H. Miller, *Trans. A. I. M. E.*, Nov., 1901.

Thiocyanate Method.

This method has many modifications and is only recommended for low grade, impure ores or tailings containing less than three per cent. of copper and particularly when the impurities are arsenic and antimony. What follows is taken largely from an article by Guess,* and the thesis of Lindeman, Columbia University, 1903.

The essential features of the method are as follows, the preliminary treatment being as already given: The filtrate containing sulphates is neutralized by ammonia and then rendered acid by either hydrochloric or sulphuric acid (1 per cent. of either is sufficient acidity), next a slight excess of sulphurous acid is added and the solution heated, then a decided excess of potassium thiocyanate † is added and the solution stirred vigorously for a couple of minutes on the water-bath; filtered immediately and washed with hot acidulated water several times. The precipitate is treated in the funnel with a hot 10 per cent. solution of sodium hydroxide, giving sodium thiocyanate, which is obtained in a clean beaker, and cuprous hydroxide which is left on the paper. This is washed by hot water. The alkaline filtrate is acidified with dilute sulphuric acid and the free hydrothiocyanic acid is titrated (warm) by potassium permanganate, according to the reaction, $10HSCN + 12KMnO_4 + 8H_2SO_4 = 6K_2SO_4 + 12MnSO_4 + 10HCN + 8H_2O$.

The theoretical factor for changing the iron standard to the copper standard is 0.1920, but it is safer to standardize against copper on account of the slight solubility of the cuprous hydroxide in caustic alkali. The results so obtained agreed with a factor of 0.1892. Of the metals likely to be present silver and possibly bismuth are the only ones which give insoluble thiocyanates under the conditions given. The silver would not interfere, for if not thrown out as chloride, the silver thiocyanide would be left with the cuprous hydroxide as it is not easily decomposed by alkali. The bismuth thiocyanate is soluble in acids and will usually be held in solution unless much is present. It is, however, precipi-

* *J. American Chem. Soc.*, 24, 708, 1902.

† Often called sulphocyanide.

tated as metallic bismuth if a large excess of sulphurous acid is used in effecting the reduction of the copper.

The weak point of the method is the precipitation of the cuprous thiocyanate, which requires careful regulation of the acidity, especially when bismuth is present. The advantages are the large quantity of permanganate used for small amounts of copper and the non-interference of arsenic and antimony.

The precipitation of copper as thiocyanate is used in alloys such as german silver, and to separate the bulk of the copper from the impurities in the analysis of pig copper.

Additional References.

Van Name. American J. Science, 163, 138–144.
Parr, J. Am. Chem. Soc., 22, 685, 1900.
Meade. J. Am. Chem. Soc., 20, 610, 1898.

CHAPTER XII.

The Determination of Lead in Ores.

The well-known inaccuracy of the fire assay for lead has rendered more important the volumetric methods for its determination. The basis for the sale of ores is now, in many cases, the percentage catually present, as shown by wet methods, minus two per cent., instead of the fire assay results.*

The methods to be described are: First, the gravimetric, weighing as sulphate; second, the ferrocyanide; third, the molybdate. While there are many other excellent methods, notably Koenig's alkalimetric, and the various modifications of the chromate, the three described are sufficient.

Gravimetric as Lead Sulphate.

Treat from 0.5 to 1 gram of the very finely ground ore, depending on the amount of lead present, with 15–20 c.c. of concentrated nitric acid and a few drops of concentrated hydrochloric acid in a small covered casserole or Erlenmeyer flask; boiling until no further solution takes place and the sulphur (if the ore is a sulphide) is completely oxidized, adding more acids if necessary to complete the decomposition. Allow to cool slightly and add about 10 c.c. of sulphuric acid 1.41 sp. gr. (1 part concentrated acid to 1 of water) and evaporate to copious, dense fumes of sulphur trioxide. All the common ores of lead will be decomposed by this treatment, which is carried out as already described under copper. The addition of a little hydrochloric acid is not always required, but usually aids in the solution of the lead. The evaporation should be nearly to dryness so as to ensure the complete conversion of lead to sulphate and also to prevent there being present too great an excess of sulphuric acid after dilution, more than 1–2 per cent.

Allow the lead sulphate, etc., to cool and add cautiously about 100 c.c. of distilled water and boil for several minutes to dissolve the ferric sulphate, etc., allow to cool and add about 15 c.c. of strong alcohol, stir well, allow to settle and decant through a small filter, leaving as much as possible of the insoluble sulphates and the silicious residue in the casserole or flask. Wash the residue

* See Iles, School of Mines Quarterly, Vol. XV., p. 336, 1894.

by decantation thoroughly with water containing 1 per cent. sulphuric acid and 10 per cent. alcohol. Pouring the washings through the filter, and wash finally with alcohol alone to remove the sulphuric acid. Place a clean beaker under the funnel, dissolve the lead sulphate from the residue in a strong hot solution of ammonium acetate, slightly acid with acetic acid; pour this solution through the filter into a clean beaker. Repeat this treatment until all the lead sulphate has dissolved; then wash the residue onto the filter and wash it finally with hot water. Most of the trouble in the determination of lead occurs just at this point; lead sulphate when free from other insoluble sulphates and freshly precipitated dissolves readily in hot ammonium acetate, but when ignited or if contaminated by barium, strontium or calcium sulphates, boiling for half an hour with a liberal excess of ammonium acetate is absolutely necessary for its complete solution. The ammonium acetate is best made by neutralizing acetic acid with ammonia as the crystallized salt is an expensive reagent and has to be used in large quantities. On solution $Pb(C_2H_3O_2)_2$ and $(NH_4)_2Pb(SO_4)_2$ are formed. The filtrate is acidified with dilute sulphuric acid, which reprecipitates the lead sulphate, alcohol is added as before (about 10 per cent.) and the precipitate filtered and washed; first with 1 per cent. sulphuric acid and 10 per cent. alcohol and finally with strong alcohol alone, either ethyl or methyl.

The ignition of the lead sulphate, when filtered on paper, gives considerable trouble and often inaccurate results because the carbon of the paper causes reduction to sulphide and sometimes to metallic lead, which requires reconversion, by nitric and sulphuric acids, to lead sulphate, often accompanied by mechanical loss. This difficulty can be overcome by using a Gooch crucible with asbestos alone, or as follows: Cut out two pieces of "acid-washed" filter paper so as to fit the bottom of the crucible accurately (using a 5 cent piece) and place them on the bottom of the crucible; then on top of these a thin layer of asbestos which has been washed with dilute sulphuric acid, making a layer of about $\frac{3}{16}$ of an inch; then, while still wet, suck this down by a strong suction as tightly as possible and dry in an oven to constant weight at 110° C. After weighing moisten the filter and then pour in the solution containing the lead sulphate, using a very gentle suction at the beginning; wash as described, dry again at 110° C. and the increased weight is lead sulphate.

This method has been thoroughly tested and will yield results (when properly carried out) which are accurate to within a few hundredths of a per cent. When such accurate work is not required the alcohol may be omitted, but the use of the Gooch crucible is strongly recommended when the necessary suction can be obtained.

Lead sulphate is slightly soluble in water and quite soluble in concentrated sulphuric acid; it is almost insoluble in a 1 per cent. solution of sulphuric acid and insoluble in alcohol. Besides being soluble in ammonium acetate it is soluble in ammonium chloride and other ammonium salts. Boiling with alkali carbonates converts it to carbonate, which can then be readily dissolved in acids. Koenig dissolves the lead carbonate in standard nitric acid and then by titrating back with a standard solution of caustic soda, using methyl orange as an indicator, determines the quantity of acid required to dissolve the lead and so finds the lead present. This method has a great advantage over the other volumetric methods in the end point, which is sharp and satisfactory, while the others are spot tests and an allowance for the excess required must be subtracted, as in the zinc titration by potassium ferrocyanide. Lead sulphate is not volatilized if present when silica is driven off by hydrofluoric and sulphuric acids.*

In some cases it is preferable to precipitate the lead as sulphide and subsequently convert it to sulphate by strong nitric acid. It should be borne in mind that lead sulphide is the most soluble of the fifth- and sixth-group sulphides in hydrochloric acid, so that less than 2 c.c. of concentrated hydrochloric acid should be present in each 100 c.c. of solution. It can also be precipitated from a neutral or alkaline solution, or one slightly acid with nitric acid. This separation is often necessary with alloys containing antimony, tin, etc., where the sixth-group metal is subsequently removed by digesting with fixed alkali sulphide.

Ferrocyanide Method.

This method is the same as the gravimetric up to the point where the lead sulphate and insoluble residue has been washed free from sulphuric acid. Add to the residue in a flask or casserole at least 15 c.c. of a solution of commercial ammonium carbonate, saturated in the cold; heat to boiling, then allow to cool, and filter through the filter already used to retain any lead sulphate from

* Meade, *J. Am. Chem. Soc.*, Vol. XIX., p. 37, 1897.

washing the lead sulphate and residue. Wash the flask and precipitate till the washings show no alkaline reaction. Place in the flask 10 c.c. of 50 per cent. acetic acid and about 20 c.c. of water and boil till the lead carbonate has dissolved completely; dilute to nearly 100 c.c., warm to 60° C., and titrate by potassium ferrocyanide, using uranium nitrate as an indicator, as with zinc.

As in the zinc titration, uniformity in the conditions for titration are essential to correct results. The same standard solution can be used, or better, one half the strength, about 10 grams of crystallized potassium ferrocyanide per liter. With such a solution the allowance for the indicator should be about 0.8 c.c.; with the stronger solution, of course, it is less. This allowance is a matter of individual eyesight and should be determined on a blank test made up of 100 c.c. of water and 10 c.c. of 50 per cent. acetic acid at a temperature of 60° C.

The standard is obtained by treating portions of pure dry lead sulphate with ammonium carbonate, dissolving the lead carbonate in acetic acid and titrating under the conditions given.

The formula of the precipitate is nearly $Pb_2Fe(CN)_6$. It does not vary as greatly with changed conditions as the zinc ferrocyanide does, but as it is much more soluble equal care must be exercised in obtaining just the conditions given. The objectionable feature is the end point. Many other indicators have been tried, but nothing better than uranium salts has been found. The good feature of the method, which is, in fact, the reason for giving it a slight preference over all the others is that the impurities likely to be present are almost without effect. Antimony even if present to the extent of 0.200 gram is absolutely without effect. Bismuth gives results slightly low, but as 0.360 gram only lowers the amount of 1 per cent. ferrocyanide used by 0.6 c.c. it will not affect results when present in small quantities. Calcium and strontium are without effect. Barium gives slightly low results. These statements are based on a series of experiments carried out exactly as the method is described here, the low results are not to be attributed to the titration but to the barium and bismuth interfering with the conversion of lead sulphate to carbonate, for this reason, in some cases, the amount of ammonium carbonate solution should be increased considerably, even up to 50 c.c., and also the time of heating.

The other metals which give insoluble ferrocyanides do not give insoluble sulphates or basic salts, so they pass into the filtrate when the lead sulphate and residue are filtered.

Molybdate Method.

This is based on the precipitation of lead as $PbMoO_4$ by a standard solution of ammonium molybdate in a hot solution slightly acid with acetic acid.* The end point is a spot test with tannin solution which turns yellow when the molybdate is in excess.

The standard ammonium molybdate is made by dissolving 9 grams of the pure salt in water and diluting to one liter; if the solution is not clear, add a few drops of ammonia. It is standardized by weighing out several portions of dry lead sulphate; dissolving them in hot ammonium acetate; adding 2–3 c.c. of acetic acid and titrating at about 90° C. till a drop of the clear solution gives a slight but distinct yellow color with a drop of a freshly prepared tannin solution, which contains about 1 gram to 300 c.c. of water. The most important point is to titrate hot. If the solution has become cool on account of slow work in titration, it should be heated again so that it is hot when the titration is finished. The solution should be decidedly acid with acetic acid. Here and also in the preceding method the plan given under zinc of dividing the solution roughly in half for titration can be utilized.

As an allowance must be made for the excess necessary to affect the indicator, uniformity in volume is essential; 200 c.c. is recommended. With this volume and the conditions given the allowance should not exceed 0.8 c.c. Many attempts have been made to obtain a more satisfactory end point for this method but so far in vain. The most satisfactory substitute has been devised by J. L. Danziger. Crystals of stannous chloride are dissolved in acetic acid till a saturated solution is formed; this is then saturated with ammonium thiocyanate. The solution so obtained gives a pink color with ammonium molybdate and is about as delicate as the tannin reaction.

To apply this method to an ore, follow the gravimetric method till the lead sulphate is dissolved in ammonium acetate, acidify with 2–3 c.c. of acetic acid, dilute to 200 c.c., heat to boiling and titrate as in standardizing.

Interferences.—Antimony and bismuth are without effect. Barium gives very low results: strontium low results: calcium very slightly low results, but not enough to affect ordinary work. As in the ferrocyanide method the action of these alkaline earth sulphates is to impede the solution of the lead, and the difficulty can

* H. H. Alexander, *Engineering and Mining Journal*, April, 1893, p. 298.

be entirely overcome by thoroughly washing the lead sulphate and then boiling it repeatedly with sufficient ammonium acetate. For comparative results on these and other methods see Bull, SCHOOL OF MINES QUARTERLY, Vol. XXIII., pp. 348–366, also *Z. für analytische Chemie*, Vol. 41, pp. 653–674, 1902.

A RESTANT SOURCE OF ERROR IN OPTICAL SUGAR ANALYSIS.*

By F. G. WIECHMANN.

The fact that the presence of the precipitate formed in clarifying sugar solutions is a source of error which may prove very considerable, has been known for many years.

Without attempting to go into the history of this matter it may be of interest to state that even in 1867 J. Welz published an article on this subject in the *Zeitschrift des Vereins für Rübenzucker Industrie*, Vol. 17, page 489. A glance through American, German, English and French publications since that time shows that this question has frequently occupied the attention of investigators of these nationalities.

In making their experiments investigators have generally followed one of two methods: that of Scheibler or that of Sachs. Scheibler's Method of Double polarization, described in the *Zeitschrift des Vereins für Rübenzucker Industrie*, 1875, Vol. 25, page 1054, is as follows: The normal weight of sugar is dissolved in distilled water; a measured amount of subacetate of lead solution is added, the volume is made up to a known volume, say 100 c.c. with water, the solution filtered and polarized.

A second solution is prepared in the same manner, except that its volume is made double the volume of the former solution; in other words, the volume of this solution is made up to 200 c.c. and this solution is then also filtered and polarized.

Assuming that the volume of the lead precipitate formed in both cases is identical, it is evident that the polarization of the more dilute solution must be somewhat less than one half the polarization of the more concentrated solution.

To make this clear, suppose the volume of the precipitate formed $= 3$ c.c. In the first case, the solution would occupy a space of $100 - 3 = 97$ c.c. In the second case, the solution would occupy a space of $97 + 100$ c.c. $= 197$ c.c.

If the polarization of the first solution (100 c.c. in volume) is equal to x polariscope-degrees, the polarization of the second solution (200 c.c. in volume) would be equal to $97/197\ x$ polariscope degrees.

* Address made at the fifth International Congress of Chemistry, Berlin.

The corrected polarization would then be found in the following manner:

Polarization of Solution A,
(100 c.c. in volume), $= 96.80$
Polarization of Solution B,
(200 c.c. in volume), $= 48.25$
$48.25 \times 2 = 96.50$
96.80
96.50
$0.30 \times 2 = 0.6$
$96.8 - 0.6 = 96.2$, Corrected Polarization.

Of course the volume of the precipitate can also readily be calculated from these data.

$$A - (B \times 2) = D, \text{ and}$$
$$\frac{D \times 200}{A + D} = \text{Volume of Precipitate.}$$

Example: $A = 96.8$
$B = 48.25$
$96.8 - (48.25 \times 2)$
$96.8 - 96.5 = 0.3$
$$\frac{0.3 \times 200}{96.8 + 0.3} = \frac{60}{97.1} = 0.6.$$

Hence the volume of this precipitate is 0.6 c.c.

This method of double polarization is, however, open to several objections. When working with raw sugar, especially with low-grade cane products, it is almost impossible to secure absolutely identical samples for comparison in the two series of observations. But even if this difficulty could be overcome, for instance by weighing out double the amount of sugar at the start, yet the doubling of the polariscope reading involves the material enlargement of any experimental error that may have been made.

To avoid the defects of this method, Francois Sachs, at the suggestion of Dr. K. Stammer, undertook to devise some other way of ascertaining the influence which the lead precipitate exerts on polarization. He published an article bearing on this subject in the

Zeitschift des Vereins für Rübenzucker Industrie, 1880, Vol. 50, p. 229.

Sachs's method consists essentially of the following: A precipitate is produced by subacetate of lead. This precipitate is washed with cold and with hot water until all of the sucrose is removed, and is then introduced into a 100-c.c. flask. A one half normal weight of pure sugar is added, dissolved, and the solution is made up to 100 c.c. with distilled water.

This solution is then well mixed, filtered and polarized and the volume of the precipitate ascertained in the following manner:

A = percentage of purity of the sucrose in the solution.

B = polarization of this solution when containing the precipitate.

V = volume of the precipitate is equal to $\frac{100\,B - 100\,A}{B}$

Example:

$$A = 99.90$$

$$B = 100.30$$

$$V = \frac{(100 \times 100.3) - (100 \times 99.9)}{100.3} = \frac{400}{100.3} = 0.4\text{c.c.}$$

In the course of this investigation, undertaken by the writer of these lines for the purpose of obtaining exact analytical data on certain cane-sugars, a number of determinations were made by both the Scheibler and the Sachs' method. In each instance only just enough subacetate of lead was used to insure a proper decolorization of the sugar solution — the slightest excess of reagent was carefully avoided.

The data secured were as follows:

Experiment No.	Grade of Sugar.	Polarization Found.	Volume of Precipitate.	Method Used.
1	Demerara Centrifugal.	96.8	0.6	Scheibler.
2	" "	96.7	0.5	Sachs.
3	San Domingo Centrifugal.	96.1	0.5	"
4	Cuba Centrifugal.	91.8	0.4	"
5	Cuba Molasses.	90.0	0.6	"
6	Jlo-Jlo Mats.	89.5	1.1	Scheibler.
7	Jamaica Muscovado.	86.8	0.3	Sachs.
8	Maceio.	86.1	0.9	"
9	Molasses.	83.1	1.0	Scheibler.
10	Cuba Muscovado.	82.7	0.7	Sachs.
11	Bahia.	76.6	1.0	Scheibler.

The results obtained exhibited such marked differences for sugars of different origin, but of approximately the same polarization, that it seemed desirable to secure additional data and, incidentally, to seek some indications as to the physical characteristics of the precipitates found in different grades of sugar.

This part of the work was carried on in the following manner:

A solution of subacetate of lead was prepared in exact accordance with the direction of the International Commission for Uniform Methods of Sugar Analysis.

A normal weight-solution of the raw sugar to be examined was then made and the minimum amount of subacetate of lead solution needed for its proper clarification was carefully determined by experiment.

The lead precipitate thus obtained was filtered on a weighed Schleicher & Schüll filter and washed with cold and with hot water until the alpha-naphthol reaction for sucrose could no longer be obtained. Then the precipitate was dried to constant weight at 100° C.

Preliminary experiments having shown that pure benzene exercised no solvent action upon the precipitate, the specific gravity of the same was determined by the aid of this reagent and then referred to the water standard. The specific gravity of the benzene employed was 0.6845.

The colonial sugars selected for these experiments embraced centrifugals from San Domingo and the Sandwich Islands, muscovadoes from the West Indies, molasses sugars from Porto Rico, concretes from San Domingo, and mats from Manila and Cebu.

The analytical data of these sugars appear in the following table:

Experiment No.	Sugar.	Polarization.	Reducing Sugars.	Water.	Ash.	Suspended Impurities.	Non-ascertained.
12	Jamaica Muscovado.	90.1	1.61	5.02	0.68	0.20	2.39
13	Maceio Muscovado.	85.4	4.35	5.60	0.75	1.06	2.84
14	San Domingo Centrifugal.	96.5	0.67	1.20	1.36	0.06	1.21
15	Sandwich Islands.	97.6	0.45	0.60	0.40	0.04	0.91
16	San Domingo Concrete.	85.2	2.91	4.92	1.68	0.30	4.99
17	Porto Rico Molasses.	88.4	3.17	3.66	1.36	0.28	3.13
18	Sandwich Islands.	89.2	1.60	2.58	2.19	0.20	4.23
19	Cebu Mats.	82.4	6.75	2.60	2.17	0.76	5.32
20	Manila Mats.	86.8	4.14	1.96	0.92	1.80	4.38

The weight, the specific gravity and the volume of the precipitates obtained from these sugars are listed below.

PRECIPITATES.

Experiment Number.	Sugar.	Weight in Grammes.	Specific Gravity $H_2O = 1{,}000$.	Volume in c.c.
12	Jamaica Muscovado.	0.4559	1.88	0.24
13	Maceio Muscovado.	0.8112	1.65	0.49
14	San Domingo Centrifugal.	0.2525	2.91	0.09
15	Sandwich Island Centrifugal.	0.1378	2.84	0.05
16	San Domingo Concrete.	1.0139	3.80	0.27
17	Porto Rico Molasses Sugar.	0.8959	4.35	0.21
18	Sandwich Islands.	1.0195	4.38	0.23
19	Cebu Mats.	1.5400	2.17	0.71
20	Manila Mats.	1.3350	2.22	0.60

Inspection of these data shows well how greatly the composition of the impurities in the different kinds of cane sugars must vary, for the specific gravities of these precipitates differ widely, from 1.65 to 4.38.

In this connection it is of interest to recall the specific gravity values obtained by Sachs of some lead salts of organic acids. Among these were the citrate, tartrate, oxalate and carbonate of lead, and their specific gravity values were found to range from 3.05 to 6.27.

Another matter of interest to be noted is the fact that the most voluminous precipitates are not always found in low-grade sugars.

Thus, precipitates almost identical in volume were obtained from sugars differing materially in quality.

No.	Polarization.	Volume of Precipitate.
12	90.1	0.24
18	89.2	0.23
17	88.4	0.21
16	85.2	0.27

To determine the extent to which polarizations might be influenced by the forming of lead compounds having specific optical properties, a complete set of parallel determinations was carried out with sugars Nos. 12–20.

In these tests a few drops of acetic acid were added after the subacetate of lead solution had been used. In only three instances however were polarization-values observed differing from those previously found, and in no instance did such difference exceed 0.1°. The former were therefore retained.

The corrected polarizations (corrected for the error caused by the presence of the lead precipitate) were calculated in the following manner:

Let: A = per cent. of sucrose in the solution.
B = polarization of this solution when containing the precipitate.
V = volume of this precipitate.

$$V = \frac{100B - 100A}{B}$$

$$BV = 100B - 100A$$

$$100A = 100B - BV$$

$$A = \frac{100B - BV}{100}$$

Example: $B = 90.10°$ Ventzke
$V = 0.24$ c.c.

$$A = \frac{(90.10 \times 100) - (90.1 \times 0.24)}{100}$$

$$A = \frac{9010 - 21.624}{100}$$

$$A = \frac{8988.376}{100} = 89.88$$

and this is the value sought.

POLARIZATION.

Experiment No.	Sugar.	Observed.	Corrected.	Diff.
1	Demerara Centrifugal.	96.80	96.22	0.58
2	" "	96.70	96.22	0.48
3	San Domingo Centrifugal.	96.10	95.62	0.48
4	Cuba Centrifugal.	91.80	91.43	0.37
5	Cuba Molasses.	90.00	89.46	0.54
6	Jlo-Jlo Mats.	89.50	88.52	0.98
7	Jamaica Muscovado.	86.80	86.54	0.26
8	Maceio.	86.10	85.33	0.77
9	Molasses.	83.10	82.27	0.83
10	Cuba Muscovado.	82.70	82.12	0.58
11	Bahia.	76.60	75.83	0.77
12	Jamaica Muscovado.	90.10	89.88	0.22
13	Maceio Muscovado.	85.40	84.98	0.42
14	San Domingo Centrifugal.	96.50	96.41	0.09
15	Sandwich Islands Centrifugal.	97.60	97.55	0.05
16	San Domingo Concrete.	85.20	84.97	0.23
17	Porto Rico Molasses Sugar.	88.40	88.21	0.19
18	Sandwich Islands.	89.20	88.99	0.21
19	Cebu Mats.	82.40	81.81	0.59
20	Manila Mats.	86.90	86.37	0.53

In these sugars, therefore, the observed error caused by the presence of the lead precipitate ranges from 0.05 to 0.98° Ventzke.

It is difficult to understand how so serious, so well-known, a defect of polariscopic analysis should have been allowed to remain unto this day.

No doubt the difficulty of determining a proper correction factor has been the chief cause of delay in seeking a remedy for this evil. Aside from this, however, there is a very general, even if a very vague impression that there are certain other sources of error inherent in the methods of saccharimetric analysis which, as it were, tend to counteract this plus error in polarization; a false sense of security has been engendered, a feeling that, after all, the results obtained will about balance in the long run.

Whatever the grounds on which such delusive reasoning may have been based in the past, to-day there is no longer any excuse for such an assumption. The analytical methods formulated by the International Commission in 1900, carefully eliminate the influence which would lower the test.

It is well known that readings of sugar solutions obtained in a saccharimeter when the saccharimeter is at a temperature above the temperature at which the instrument has been graduated, are slightly lower than are the readings of such solutions when obtained at the graduation-temperature of the instrument.

This phenomenon is due to the influence which an elevation of temperature exercises in the quartz wedges of the saccharimeter — these quartz-wedges are expanded by a rise in temperature.

This cause of disturbance can and, of course, should be wholly eliminated by adjusting the saccharimeter with a pure sugar solution, at the temperature at which the readings are to be made. Or, if numerous sugar solutions are to be tested at various temperatures it may perhaps prove more convenient to make the necessary correction for this error by calculation.

This is effected by use of the so-called Jobin formula, which reads:

$$\text{Polarization} + (0.00016\ T)\ N.$$

In this formula T stands for the difference in temperature at which the sugar solution is prepared and polarized, and the temperature at which the saccharimeter has been graduated; N stands for the saccharimeter degrees of the sugar solution examined.

In the commercial analysis of sugars, this correction is generally not made. It is not made because it is held to offset — in a measure — the plus error due to the presence of the lead precipitate in the solution.

That the one error will, in part, counterbalance the other is obvious. It seemed, however, of interest to learn something of the actual numerical relations existing between the two.

To gain this information it was necessary to obtain reliable temperature data as a basis.

The mean annual temperature for Boston, New York, Philadelphia and San Francisco, four of the principal ports of entry for sugar in the United States of America, was in:

	In 1901.	In 1902.
Boston,	9.45° C.	9.78° C.
New York,	11.28	11.45
Philadelphia,	12.11	12.33
San Francisco,	12.89	13.00

For these data the writer is indebted to the courtesy of the U. S. Weather Bureau, at Washington, D. C.

All of these temperatures are considerably below 20° C., the standard temperature adopted by the International Commission for the graduation of saccharimeters. The actual temperature conditions under which polariscopic determinations of sugars are made of course differ materially from these temperatures.

In order to obtain accurate data on this point the writer caused three observations a day to be made in his laboratory, at 8 A. M., at 12 M., and at 3 P. M. These observations were carried on for two years during 1901 and 1902. The averages of these observations, monthly and annual, are noted in the following table:

	1901.	1902.	1903.
January,		22.4	22.4
February,	21.0	21.6	
March,	22.5	22.6	
April,	22.4	23.1	
May,	22.3	23.5	
June,	26.0	26.0	
July,	27.7	27.7	
August,	27.9	27.2	
September,	26.0	25.6	
October,	23.3	23.7	
November,	22.7	23.1	
December,	23.5	22.1	
Average	24.12	24.05	

Although fluctuations are to be noted in some of the corresponding months in the two years, yet there is not 0.1° C. difference between the mean annual averages of the two years. In 1901 for eleven months this value was 24.12° C., in 1902 it was 24.05° C. It will therefore be practically correct to say that all tests made in both of these years were made at a temperature — on an average — of 4.1° C. above the standard temperature of 20° C.

Referring to Jobins' formula it will be seen that the correction to be applied for 4.1° Centigrade temperature is calculated by the expression:

$$0.000656 \times \text{Degrees Ventzke.}$$

Doing this the following correction-factors result:

Experiment No.	Degree Ventzke.	Experiment No.	Degree Ventzke.
1	0.063	11	0.050
2	0.063	12	0.059
3	0.063	13	0.056
4	0.060	14	0.063
5	0.059	15	0.064
6	0.059	16	0.056
7	0.057	17	0.058
8	0.056	18	0.058
9	0.054	19	0.054
10	0.054	20	0.057

As in these experiments the saccharimeter was purposely not adjusted for the higher temperature (average = 24.1° C.) the observed volume-error, caused by the presence of the lead precipitate, has already been diminished by the quartz-wedge error;

Experiment No.	Plus Error.	Minus Error.	Excess of Plus Error.
1	0.643	0.063	0.580
2	0.543	0.063	0.480
3	0.543	0.063	0.480
4	0.430	0.060	0.370
5	0.599	0.059	0.540
6	1.039	0.059	0.980
7	0.317	0.057	0.260
8	0.826	0.056	0.770
9	0.884	0.054	0.830
10	0.634	0.054	0.580
11	0.820	0.050	0.770
12	0.279	0.059	0.220
13	0.476	0.056	0.420
14	0.153	0.063	0.090
15	0.114	0.064	0.050
16	0.286	0.056	0.230
17	0.248	0.058	0.190
18	0.268	0.058	0.210
19	0.644	0.054	0.590
20	0.587	0.057	0.530

the former, the plus error, must therefore be increased by the amounts just calculated in order to learn its true extent.

This leads to the following data:

Inspection of these figures shows, that — considering all results — the plus error exceeds the minus error by from 0.05° to 0.98° Ventzke, on an average by 0.46° Ventzke.

If the data secured by the Scheibler method (Nos. 1, 6, 9, 11) be eliminated as possibly not equally trustworthy with the rest, then the plus error is found to exceed the minus error by from 0.05° to 0.77° Ventzke, on an average by 0.38° Ventzke.

The practice universally followed in commercial sugar testing — at least up to the introduction of the methods of the International Commission in 1900 — the ignoring of the quartz-wedge error because allowance is not made for the error induced by the presence of the lead precipitate, is thus seen to be perfectly justified by the actual state of affairs.

In fact, as matters stand at present, it is evident that the commission's regulations guarding, as they most properly do, against a lowering of test by the influence of temperature on the quartz-wedges of the polariscope, aggravate, unintentionally, it is true, but nevertheless effectively, the evil resulting from the presence of the lead precipitate formed in clarifying the solution.

It will be remembered that the average excess of the plus error over the minus error was found to be 0.38° Ventzke. In commercial practice this figure would rather be apt to be higher than lower, for whereas in these experiments scrupulous care was taken to avoid all excessive additions of clarifying reagents, such care and precaution would and could hardly be taken in ordinary routine work.

On the other hand, the grade of raw cane sugars received would vary considerably in different years. If high-grade sugars should predominate the magnitude of the volume-error would be decreased, if low-grade sugars were purchased in greater quantity than usual, the error would assume larger proportions.

Considering all things, it will probably be rather below than above the truth to assume 0.25° Ventzke as the average plus factor of error caused in cane-sugars by the presence of the lead precipitate.

This error also affects beet products, but to a less degree; Scheibler in 1875, evaluated it at 0.15 per cent. to 0.20 per cent.,

with a leaning toward the lower figure. This emphasizes the conservativeness of the figure 0.25 per cent. at which the writer has placed it for cane sugars; as before said, in all probability the error is greater than this.

But whatever the extent of the error, the harm it works seems of sufficient importance to call for immediate and careful consideration with a view to its abatement.

Broadly speaking, two courses present themselves which might be followed to achieve this purpose.

On the one hand, the extent of the error, under various conditions, might be determined and a correction therefor introduced. On the other hand, search might be made for some reagent or reagents whereby decolorization of sugar solutions could be secured without the formation of any precipitate and, of course, without affecting the optical properties of the sucrose solution.

Either course, whichever might be chosen, would necessitate a very considerable amount of work; of this the writer is thoroughly aware from his own tentative efforts along both of these lines of investigation.

Still, "before there can be applied science, there must be science to apply." It would therefore seem most proper to place this matter officially before the International Commission for Uniform Methods of Sugar Analysis.

This the writer would hereby do, and, in so doing, he would express the hope that this International Commission will charge itself with the devising and the introduction of a method in which this grave defect may be entirely avoided, a method to which the imprimatur of this commission may unhesitatingly be given.

FORMULÆ FOR CALCULATING THE SIZE OF WIRE ROPES.

By SHELDON SMILLIE.

The subject of wire ropes is one which interests almost every kind of man engaged in construction work from the plain contractor with his jib derrick to the engineer who wants to know what size rope to use in bridge construction or to hoist a heavy load from a deep mine. It has surprised me upon looking over the numerous handbooks for the use of students that there are practically no formulæ given for calculating the size of rope to withstand a given strain, dependence being laid on tables in which the size is found after several substitutions. By the use of the tables published by J. A. Roebling's Sons Co., I have been able to deduce several empirical formulæ which I have tried numerous times and have found them to give precisely the same results as the table after several operations.

It is close enough to say that the load carried by metal rope is proportional to the area of the circle described on its greatest diameter.

So let

d = the diameter of rope to be found,

W = the load to be carried in pounds,

K = the maximum load held by a 1″ rope,

and

$\frac{\pi}{4} d^2$ = the area of the circumscribed circle.

By the rule of the proportion of loads and areas: area of diameter = 1 : maximum load held by 1″ rope

$$:: \frac{\pi}{4} d^2 : W,$$

or

$$\frac{\pi}{4} : K :: \frac{\pi}{4} d^2 : W.$$

Solving

$$d = \sqrt{\frac{W}{K}}.$$

If f is the factor for safety we have for the safe load held by any rope

$$d = \sqrt{\frac{Wf}{K}}.$$

Substituting the values of K given by the various manufacturers the following series of formulæ are derived.

For ropes composed of 6 strands, 19 wires each:

for Swedish Iron $$d = \sqrt{\frac{Wf}{34{,}000}}, \quad (1)$$

for Cast Steel $$d = \sqrt{\frac{Wf}{68{,}000}}, \quad (2)$$

for Crucible Cast Steel $$d = \sqrt{\frac{Wf}{78{,}000}}, \quad (3)$$

for Plow Steel $$d = \sqrt{\frac{Wf}{88{,}000}}. \quad (4)$$

For ropes composed of 6 strands, 7 wires each, we get:

for Swedish Iron $$d = \sqrt{\frac{Wf}{32{,}000}}, \quad (5)$$

for Cast Steel $$d = \sqrt{\frac{Wf}{64{,}000}}, \quad (6)$$

for Crucible Cast Steel $$d = \sqrt{\frac{Wf}{74{,}000}}, \quad (7)$$

for Plow Steel $$d = \sqrt{\frac{Wf}{84{,}000}}. \quad (8)$$

Introducing the usual factor of safety of 5 and removing the integers from under the radical:

equation (1) becomes $d = 0.0121 \sqrt{W}, \quad (1a)$

" (2) " $d = 0.00858 \sqrt{W}, \quad (2a)$

" (3) " $d = 0.00801 \sqrt{W}, \quad (3a)$

" (4) " $d = 0.00753 \sqrt{W}, \quad (4a)$

" (5) " $d = 0.01250\sqrt{W},$ (5a)

" (6) " $d = 0.00884\sqrt{W},$ (6a)

" (7) " $d = 0.00822\sqrt{W},$ (7a)

" (8) " $d = 0.00772\sqrt{W}.$ (8a)

These formulæ are similar to those given by the manufacturers themselves but are of value only for small work where the weight of the rope is negligible. In deep mine work however where the weight of the rope may be as great or greater than the load hoisted other relations must be found. In the case of hoisting a load with six inches slack it has been found that the effect of the load is doubled so

$$W = 2L + aD.$$

where L is the load, a is the weight per foot of the rope and D is the greatest distance from the load to the pulley or sheave.

If this were substituted there would be two unknown quantities and the equation impossible of solution. So it is necessary to find a relation between a and d. To do this I plotted a curve taking the diameters as ordinates and the weights per foot as abscissæ. The equation of this curve I found to be

$$d^2 = \frac{2a}{\pi}$$

or

$$a = \frac{\pi d^2}{2},$$

which being introduced gives

$$W = 2L + \frac{D\pi d^2}{2}.$$

Substituting this in the general equation of d gives

$$d = \sqrt{\frac{2Lf}{K - \frac{\pi}{2}Df}}.$$

Inserting the values of K and taking the ropes in the same order as before the following series results:

For 6 strands, 19 wires each:

$$d = \sqrt{\frac{L}{\frac{17{,}000}{f} - .786D}}, \qquad (1b)$$

$$d = \sqrt{\frac{L}{\frac{34{,}000}{f} - .786D}}, \qquad (2b)$$

$$d = \sqrt{\frac{L}{\frac{39{,}000}{f} - .786D}}, \qquad (3b)$$

$$d = \sqrt{\frac{L}{\frac{44{,}000}{f} - .786D}}. \qquad (4b)$$

For haulage rope of 6 strands, 7 wires each :

$$d = \sqrt{\frac{L}{\frac{16{,}000}{f} - .786D}}, \qquad (5b)$$

$$d = \sqrt{\frac{L}{\frac{32{,}000}{f} - .786D}}, \qquad (6b)$$

$$d = \sqrt{\frac{L}{\frac{37{,}000}{f} - .786D}}, \qquad (7b)$$

$$d = \sqrt{\frac{L}{\frac{42{,}000}{f} - .786D}}. \qquad (8b)$$

Where the load is always suspended from the rope, as in elevator practice or the counter-weight for skip or cage, the factor of 2 is omitted and the general formula is

$$d = \sqrt{\frac{Lf}{K - \frac{\pi}{2}Df}}.$$

Example. — What size plow-steel haulage-rope shall I use to raise 3,150 pounds from a depth of 2,000 feet, using a safety factor of 5? Substitute values in (4c).

$$d = \sqrt{\frac{3{,}150}{\frac{42{,}000}{5} - 1{,}570}} = \surd.46 + = .68''.$$

An eleven-sixteenth inch rope is .69″ in diameter.

The strength of lock coil rope varies by the same rule although not as closely as the ordinary rope but near enough to give correct results. Similarly the weight per foot varies by the equation.

$$d^2 = \frac{2a}{5},$$

$$a = \frac{5d^2}{2}.$$

For hoisting with slack

$$W = 2L + 2.5d^2D.$$

Whence

$$d = \sqrt{\frac{2L}{\frac{K}{f} - 2.5D}}.$$

K being 86,000 pounds,

$$d = \sqrt{\frac{L}{\frac{43{,}000}{f} - 1.25D}}. \qquad (9)$$

If the rope is always taut,

$$d = \sqrt{\frac{L}{\frac{86{,}000}{f} - 2.5D}}. \qquad (9a)$$

The foregoing formulæ apply to vertical hoisting only. To determine the size of rope required to hoist at an angle multiply the quantity under the radical by the sine of the angle.

NOTE.—The writer is indebted to Prof. H. S. Monroe and Mr. Kurtz of the Mining Department for their kind criticism of the foregoing.

A METHOD FOR THE EXACT EXPRESSION OF CRYSTAL HABIT.

By AUSTIN F. ROGERS.

It is generally recognized that certain laws govern crystal habit, but up to the present time no one has succeeded in discovering such laws.* There is reason to think that within the next few years interest in this question will be aroused and that there will be an attempt on the part of crystallographers to determine these laws or at least to learn more of the habit of crystals. Any serious study of crystal habit involves the use of a method of expressing crystal habit mathematically. The following method is suggested:

The morphological constants of crystal, *i. e.*, the axial elements, the indices and the interfacial (or coördinate) angles may be determined and expressed in exact mathematical language, but as far as known there has been no attempt of treating crystal habit in the same way. A number of crystals may have exactly the same axial elements, their faces the same indices and the same angles between the faces and yet differ greatly in the relative development of their faces or in other words, the crystal habit is entirely different. This fact is brought out in Fig. 4. A verbal description or figure conveys some idea of the habit of a crystal. Thus we say a crystal is prismatic, short prismatic, long prismatic tabular, thin tabular, or thick tabular, etc. But these terms do not convey any *exact* idea of the habit, though in most cases they may give an adequate idea. Two crystals may be described as tabular yet differ vastly in the relative development of their faces. Figures are better than verbal descriptions but it is not always convenient to represent them, and in any case the figure needs a mathematical supplement as to the habit just as the faces, angles, etc., do. While figures and verbal descriptions may suffice for all ordinary purposes, yet in some kinds of work (especially any work on crystal habit itself) it may be convenient and desirable to indicate the habit in exact language just as we do the indices, angles, elements, etc.

Parallel planes are crystallographically equivalent and are usually denoted by the same Miller indices. But by means of the Miller indices we may also designate non-identical parallel planes.

* Given certain crystal faces, Goldschmidt has found that certain laws govern the occurrence of other faces. *Zeit. f. Kryst.*, 28, 1, and 441, 1897.

For example Fig. 1 represents the orthographic projection of a portion of an orthorhombic crystal. The plane cutting a, b at unit distances is (110). Planes cutting the axes at $\frac{1}{2}a$, $\frac{1}{2}b$, and at $\frac{1}{3}a$, $\frac{1}{3}b$ are respectively (220) and (330). Similarly the dotted lines in Fig. 2 represent the planes (020) and (050). Fig 3 represents a tetragonal crystal $z\{101\}$, $c\{001\}$. The habit is $z\{101\}$, $c\{002\}$. The dotted plane is $c\{004\}$. Instead of these we may write 110 $=(110)^1$; $(220)=(110)^2$; $(330)=(110)^3$; $(020)=(010)^2$: $(050)=(010)^5$ in which the ordinary symbol and an exponent indicating the habit are given together. Or instead we may place the small exponent with the letter for the face. For instance if m is (110), the planes in Fig. 1 may be m^2 and m^3 in place of $(110)^2$

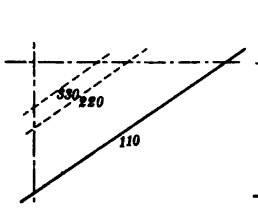


FIG. 1.

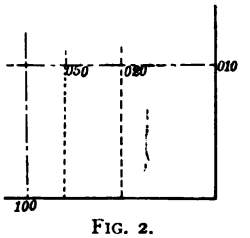


FIG. 2.

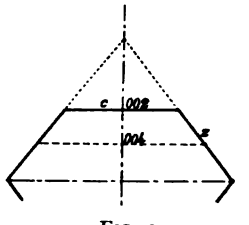


FIG. 3.

and $(110)^5$. According to this method the crystal in Fig. 3 would be expressed thus: habit, zc^2. Another more complex crystal might be: habit, $ma^2b^3z^{1.5}$. The habit symbol as we may call such an expression gives no definite idea of the habit directly but it is to be noted that the larger the exponent of the letter of the symbol the more prominent is the face represented by the letter. Fig. 4 illustrates this point. The habit varies from $mb^{1.1}$ to mb^{10}. The larger the exponent of b, the more prominent is the face b.

The method consists in obtaining the dimensions of the crystal or its faces in certain definite directions. For example in the or-

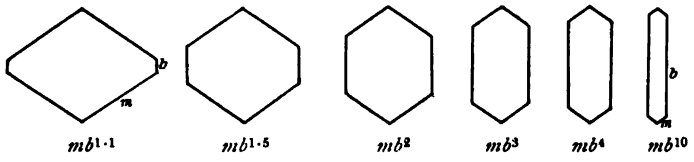


FIG. 4.

thorhombic crystal represented in orthographic projection by Fig. 5, $a:b:c = 0.5:1:1.33$; $m\{110\}$ $c\{001\}$ $b\{010\}$. x, y, z measured $= 6$, 10 and 8 mm. respectively; y, which should be 12 mm., is only 10 mm. Then $12 \div 10 = 1.2$. z should be 16 mm. ($1.33/0.5 \times 6$)

but is only 8 mm., then $16 \div 8 = 2$. Therefore taking $m\{110\}$ as unity we have as the habit symbol $mb^{1.2}c^2$. Fig. 6 represents another example, a tetragonal crystal, $m\{110\}$ $z\{111\}$. $\dot{c} = 0.66$. v, w measured = 6 and 10 mm. respectively. Taking $z\{111\}$ as

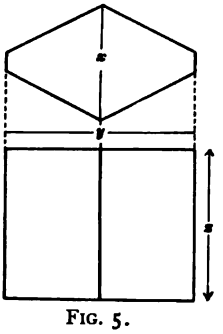


FIG. 5.

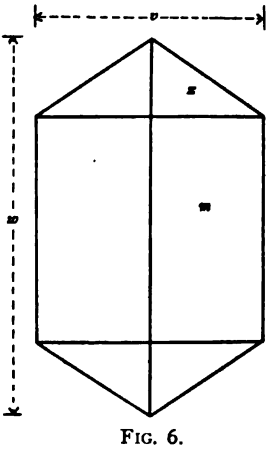


FIG. 6.

unity, v, which is 6 mm., should be 15 mm. (10/0.66). Then $15 \div 6 = 2.5$. Therefore the habit symbol is $zm^{2.5}$.

Fig. 7 represents a monoclinic crystal, orthoclase (see Fig. 21), $m\{110\}$ $b\{010\}$ $c\{001\}$ $y\{\bar{2}01\}$. Take m as unity. Measured in the direction of the $\dot{a}$-axis, the crystal is 28 mm.; in the direction of the

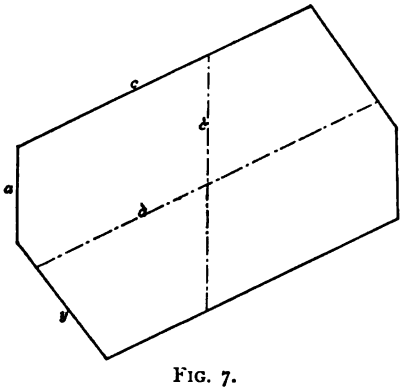


FIG. 7.

$\dot{c}$-axis it is 17 mm. but should be for unity 23.6 mm. [0.658 ($\dot{a}$) : 0.555 ($\dot{c}$) :: 28 : 23.6]. Then $23.6 \div 17 = 1.39$. Therefore $c^{1.39}$. In the direction of the $\bar{b}$-axis it measures 16 mm. but should be for unity 42.55 mm. [0.658 : 1 :: 28 : 42.55]. Then $42.55 \div 16 = 2.66$.

Therefore $b^{3.66}$. Along the edge a it measures 6 mm. and along y, 9.5 mm. By a graphical determination it is found that y is $y^{0.57}$. Therefore the habit symbol is $mc^{1.30}b^{3.66}y^{0.57}$.

It must be confessed that there are a number of practical difficulties which naturally limit the number of crystals which can be determined in this way. In the case of singly terminated crystals only a partial expression of the habit can be obtained. Complex crystals are difficult to deal with but the habit is largely determined by prominent faces with simple indices and smaller faces may be neglected. Imperfections and distortions may be averaged but in certain cases they do not interfere.

The question as to whether or not the habit symbols are rational numbers was suggested by Professor Moses but apparently this question must be answered negatively as will be seen in the following examples.

Examples.

Zircon.

Cheyenne Cañon, El Paso Co., Col. $z\{111\}$, $m\{110\}$, Fig. 8. The average of 5 determinations varying from $zm^{1.08}$ to $zm^{1.12}$ gave the habit symbol $zm^{1.1}$.

Buncombe Co., N. C. z, m, Fig. 9. The average of 14 de-

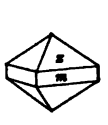


Fig. 8.

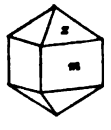


Fig. 9.

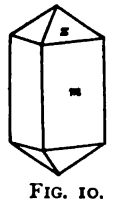


Fig. 10.

Fig. 11.

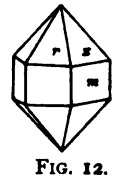


Fig. 12.

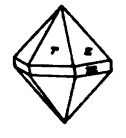


Fig. 13.

terminations varying from $zm^{1.35}$ to $zm^{2.2}$ gave the habit symbol $zm^{1.6}$.

St. Lawrence Co., N. Y. z, m, Fig. 10. The average of 5 determinations varying from $zm^{4.21}$ to $zm^{4.87}$ gave as the habit symbol $zm^{4.51}$.

Quartz.

Warsten, Westphalia. $r\{10\bar{1}1\}$, $z\{0110\}$, $m\{10\bar{1}0\}$, Fig. 11. The average of 6 determinations varying from $rzm^{1.5}$ to $rzm^{1.7}$ gave $rzm^{1.6}$.

Middleville, Herkimer Co., N. Y. r,z,m, Fig. 12. The average of 12 determinations varying from $rzm^{1.15}$ to $rzm^{1.54}$ gave $rzm^{1.34}$.

Cumberland, Eng. rzm, Fig 13. The average of 3 determinations varying from $rzm^{1.05}$ to $rzm^{1.13}$ gave $rzm^{1.09}$.

Apophyllite.

Bergen Hill, N. J. $a\{100\}$, $c\{001\}$, pseudo-cubic crystals, Fig. 14. Average of 5 varying from $ac^{1.42}$ to $ac^{1.52}$ gave $ac^{1.45}$.

Guanajuato, Mexico. a, c, long crystals. Fig. 15. Average of 9 varying from $ac^{0.34}$ to $ac^{0.55}$ gave $ac^{0.42}$.

Wulfenite.

Yuma Co., Ariz. $u\{102\}$, $c\{001\}$, tabular crystals, Fig. 16. Average of 6, varying from $uc^{3.23}$ to $uc^{4.00}$ gave $uc^{3.5}$.

Calcite.

Cumberland, Eng. $m\{10\bar{1}0\}$, $e\{01\bar{1}2\}$, Fig. 17. The average of 8 determinations varying from $em^{1.10}$ to $em^{1.31}$ gave $em^{1.25}$.

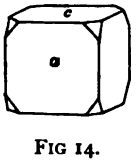


FIG 14.

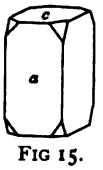


FIG 15.

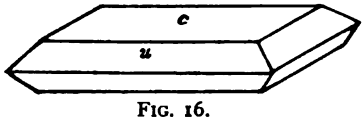


FIG. 16.

FIG. 17.

Aragonite.

Bilin, Bohemia. $m\{110\}$, $b\{010\}$, $k\{011\}$, Fig. 18. The average of 3 determinations varying from $mb^{2.2}k^{?}$ to $mb^{2.4}k^{?}$ gave $mb^{2.31}k^{?}$. *

Apatite.

Ehrenfriedensdorf, Saxony. $c\{0001\}$, $m\{10\bar{1}0\}$, Fig. 19. Average of 5 determinations varying from $ac^{1.22}$to $ac^{1.6}$ gave $ac^{1.37}$.

FIG. 18.

FIG. 19.

FIG. 20.

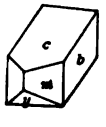


FIG. 21.

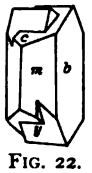


FIG. 22.

Staurolite.

Lisbon, N. H. $b\{010\}$, $m\{110\}$, $c\{001\}$, Fig. 20. Determinations gave $mc^{0.5}b^{1.11}$; $mc^{0.92}b^{1.11}$; $mc^{0.54}b^{0.93}$; $mc^{0.61}b^{1.4}$; $mc^{0.63}b^{1.2}$.

Orthoclase.

Robinson, Col. $m\{110\}$, $b\{010\}$, $c\{001\}$, $y\{201\}$, Fig. 21.
Three determinations, $mc^{1.39}b^{2.66}y^{0.57}$; $mc^{1.36}b^{3.45}y^{0.57}mc^{1.68}b^{3.04}y^{0.42}$.
Breckenridge, Col. m, b, c, y, Carlsbad twins, Fig. 22.
Two determinations, $mc^{0.87}b^{3.25}y^{0.48}$; $mc^{0.87}b^{3.44}y^{0.47}$.

* As the crystals are singly terminated the complete habit symbol can not be btained.

UNVEILING OF A BRONZE TABLET IN HAVEMEYER HALL TO THE MEMORY OF HAMILTON YOUNG CASTNER, DECEMBER 16, 1902.

ADDRESS OF PROFESSOR CHANDLER.

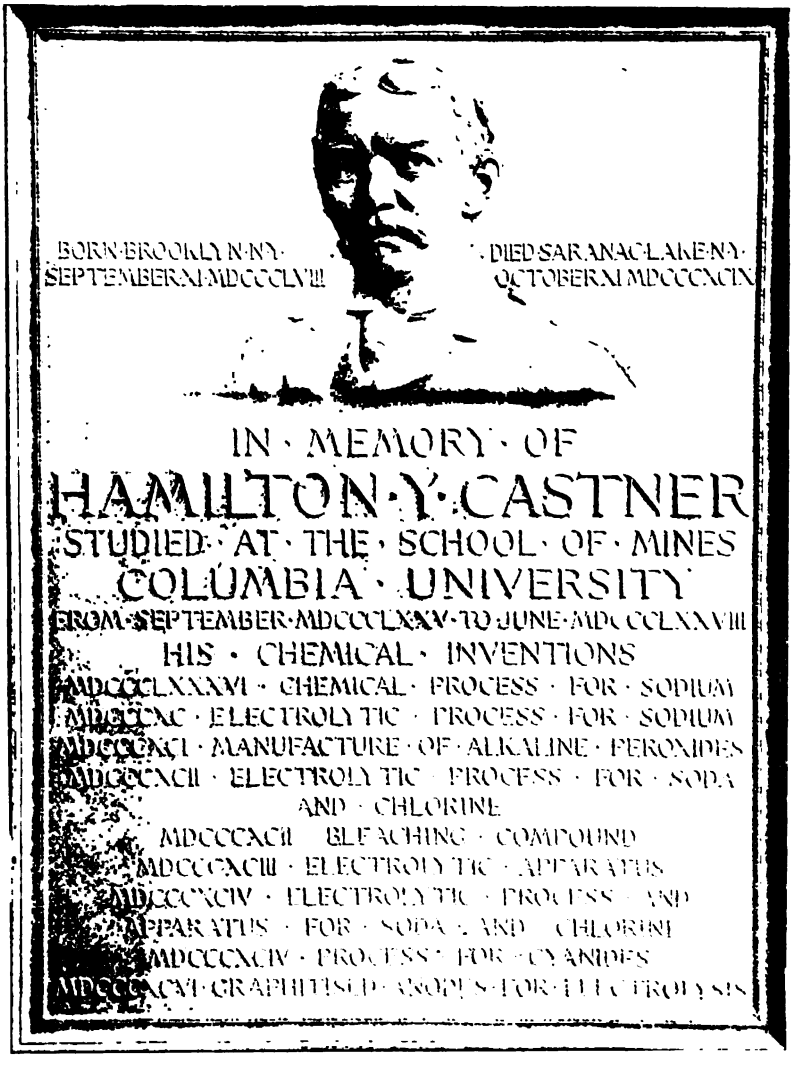
We have gathered here, my friends, to do honor to the memory of one of the most distinguished pupils who has ever gone out from this School of Mines of Columbia University. President Butler was to have presided at this meeting, but illness in his family makes it impossible. In honoring Mr. Castner we are honoring our university. We may take great satisfaction in the thought that we have been able to assist in educating a man who has accomplished so much in the applications of chemistry to the benefits of the human race.

The inventor is like the poet, he is born and not made. The inventive quality is something which resides in the personality of the individual. We cannot make inventors; we can assist inventors; we can give them information, enlarge their stock of material, add to their supply of tools, complete their equipment, but the originality is born in the man.

The reason we are placing on the walls of Havemeyer Hall a memorial tablet of Hamilton Y. Castner is because, as we look over the list of the pupils of the School of Mines since 1864, when it was first opened, we find that he ranks among the most distinguished of the men who have gone out from this school.

I may say that the idea of placing a memorial tablet at Columbia in honor of Mr. Castner originated with several of his friends who had known him through all his struggles and efforts to develop his inventions and bring them to practical success. These friends wished to do something to perpetuate his memory, so that after those who have known him personally have passed away, his memory may still remain fresh, to encourage the generations of young men who will frequent these halls. It was first suggested to erect a monument, perhaps at the cemetery, at his grave, but it was finally thought far more profitable to place it in the institution where he received his professional instruction, which aided him in making his work a success.

Hamilton Y. Castner was born in Brooklyn on the 11th of September, 1858. He pursued his early studies in the city of Brooklyn, and prepared himself for admisson to the School of Mines in the Brooklyn Polytechnic Institute. He came to the School of



Mines in September, 1875, entering as a regular student in the the course of analytical and applied chemistry. But he was very anxious to begin his life work and looked forward to devoting four continuous years to the study of the various branches required for

the degree with impatience; and after spending a year in the regular course, decided that he much preferred to abridge the time and devote his energies to such branches of chemistry as were likely to prove most useful to him. For this reason he became a special student, and while pursuing most of the course, he dropped some subjects which are regularly required for the degree. As a result of this, instead of remaining four years, he left in 1878, having studied for three years, and entered at once upon the practice of his profession.

The first effort he made which indicated his originality was the *electrical* process for manufacturing animal charcoal. It had been customary up to this time in preparing animal charcoal for sugar refining to waste all the volatile products of the distillation. It occurred to Mr. Castner that it was quite possible to obtain as great a yield of charcoal and yet utilize the waste products. His first invention had this for its object. It was successful as far as it went, but the manufacturers of animal charcoal had their plants well organized, and I do not know whether his improvements ever went into practice.

His great successes came when he began to devise new and improved methods for preparing alkaline products and utilizing them for purposes not possible before.

His first invention in this direction was a process for manufacturing metallic sodium. Sodium had been discovered in 1807 by Sir Humphrey Davy. Subsequently, methods were devised for preparing it from carbonate of soda and charcoal, but this was very expensive because of the high temperature required in its preparation. The apparatus was rapidly destroyed, thus making the sodium so expensive that it was not available for practical purposes, useful as it would have been had not the cost of its manufacture made its use almost prohibitive.

No great efforts were made to manufacture sodium on a large scale until 1851, when St. Clair Deville, of Paris, attempted to establish a great aluminium industry. Louis Napoleon furnished several million francs from the treasury of France, large works were erected, and some of the great chemists of France attempted to devise a method by which aluminium could be made available for general use.

St. Clair Deville found the only practical method of making aluminium was by means of metallic sodium. It may be said that

the best chemists in Europe had devoted more or less attention to efforts to make metallic sodium. Not one succeeded in making any sodium which could be marketed for less than two dollars and a half per pound; and as it took three pounds of sodium to manufacture one pound of aluminium, the cost for metallic sodium alone would be $7.50 per pound of aluminium produced by its use.

So the idea of St. Clair Deville and Louis Napoleon of giving to the world the new metal aluminium for every-day use was never realized, simply because they could not devise a cheap method of making sodium.

This was one of the first problems to which Mr. Castner devoted his attention, and he was wonderfully successful. He first invented a chemical process, which was a great success, and produced sodium at a very small price; in fact, so small a price that he immediately captured the entire market for aluminium, as he was able by means of his cheap sodium to supply aluminium at a low price.

I have been informed that before Mr. Castner began to manufacture aluminium the lowest price at which it had been sold was $10.00 per pound, and when Castner devised his sodium process he was able to manufacture aluminium at a cost of $1.00 per pound.

This revolutionized the whole industry, and aluminium could now be used for a hundred different purposes.

This process of Castner's is an extremely beautiful one, and it is a marvel that when Friedrich Woehler, of Goettingen, St. Clair Deville, of France, and many other distinguished chemists had sought for years to devise a method of making cheap sodium not one of them had ever succeeded in working out Castner's method.

Castner threw aside the old processes and made a new departure entirely. He substituted for the charcoal, carbide of iron. The difficulty had been, when attempts were made to use caustic soda, that the charcoal used, being lighter than the soda, floated on the surface and failed to effect its reduction. Castner used carbide of iron as a reducing agent, finding that the carbide of iron in the mixture had about the same specific gravity as caustic soda.

This process was beautiful and could be worked at a very moderate temperature. He used steel crucibles, six feet in diameter, and the temperature required being so low, the same crucible could be used more than a hundred times. These enormous crucibles were placed in suitable furnaces, each filled with the mixture, and

exposed to the proper heat, and the process of manufacture of sodium became as simple as the manufacture of iron, and the cost, instead of being two and a half dollars became about twenty-eight cents a pound.

This great success in reducing the price of sodium made it possible to make aluminium at a moderate cost. Castner immediately formed an aluminium company in London, and large works were erected near Birmingham to manufacture sodium and aluminium. Thus, for the first time since its discovery in 1827 by Woehler, aluminium was supplied at a price which made it possible to utilize it for practical purposes.

Everything went on with the greatest regularity and satisfaction, until one of those catastrophies liable to overtake every inventor occurred. Another chemist invented another process still cheaper. Charles M. Hall, of Niagara Falls, invented a new and radically different process of making aluminium without the aid of sodium. By it the aluminium could be produced at a lower price than by Castner's method, and consequently Hall took the market away from Mr. Castner. This does not detract in any way from Mr. Castner's inventive genius in inventing his beautiful process.

Now Mr. Castner found himself at the head of an enormous establishment designed for the manufacture of aluminium, with a large company and a large capital, and the ground cut from under his feet by another inventor. He then turned his attention to utilizing his sodium for other purposes and in this he was extremely successful.

It first occurred to him that sodium was very valuable for use in the manufacture of some of the new remedies, the valuable medicinal preparations made from coal tar, and his sodium was employed in the manufacture of other drugs which have proved so useful in modern medicine.

Then it occured to him that he might use his metallic sodium for the production of peroxide of sodium, and this could be used for the manufacture of hydrogen peroxide for bleaching purposes, for bleaching feathers and other delicate fabrics. So he invented a process for converting his metallic sodium into peroxide of sodium.

Then it occurred to him that having this cheap sodium he could apply it for the preparation of pure cyanides. It had been

extremely difficult to furnish cyanide with anything like a reasonable purity, the commercial cyanides containing only 50, 60 or 70 per cent pure cyanide, the rest being impurities. Castner found that he could produce pure cyanide of potassium at a price no greater than the impure had formerly cost. He immediately enlarged his establishment and manufactured pure cyanides, cyanide of potassium, and cyanide of sodium.

These were employed largely in electro-plating and gilding and the electro-depositing of brass and various other metals. They found still greater application in the extraction of gold from low grade ores, a process used now from one end of the world to the other. Enormous quantities are used in South Africa for extracting gold, and also in California.

These are some of the purposes for which his cheap sodium is used.

But Castner was not satisfied. True, he had invented a process for metallic sodium at a price one eighth or one tenth the price at which it had been sold previously, but he still continued to devote his mind to the discovery of a better process; and so he invented the electrolytic process, which was better than the chemical one. That was founded on the process of Sir Humphrey Davy, who first discovered sodium in 1807.

At that time Sir Humphrey Davy received a present of an enormous galvanic battery and began to apply the galvanic current as an agent for reducing chemical compounds into their component parts, a current of electricity having the property of tearing elements away from each other or isolating them.

It had been the assumption for many years that the alkalies all contained metals, but no one had ever seen the metals; they are never found in nature, and no one had ever devised a process by which any one of their compounds could be compelled to give up its metallic constituent. For this purpose Sir Humphrey Davy applied his battery to the electrical decomposition of the caustic alkalies.

He first tried a solution, such as common salt or some other compound of sodium, as caustic soda. He had no difficulty in bringing about the decomposition, but the metal never showed itself; liberated from one compound it attacked the water present and produced another. He could only infer that the metal was set free, because the water was decomposed.

It then occurred to Sir Humphrey Davy, that as he could not isolate these metals from their compounds when dissolved in water, he might isolate them in the absence of water, so he undertook to decompose dry caustic soda by electrolysis. He selected a piece of caustic soda and brought the electrodes in contact with it and turned on the current. But nothing happened, because caustic soda is a non-conductor of electricity and no current passed through it. But shortly the moisture of the air which gathered upon the soda produced a film of soda lye which carried a little current of electricity; the resistance developed heat; the caustic soda solution began to warm up; that caused the caustic soda to melt; the melted caustic soda carried the current, and, to the great delight of Sir Humphrey Davy, a little metallic sodium was liberated in metallic globules, thereby verifying the theory that salt and all compounds which contain soda were really compounds of a metal, sodium.

Davy never succeeded in preparing sodium in any quantity The difficulties of this method were so great that no one ever prepared any quantity of metal by this process. No one ever found out a method of practicing successfully the electric process, so the chemical methods were thought out, and Castner's beautiful chemical process of making sodium was the most successful of them all.

Now Castner studied the electrolysis of caustic soda; he found out what the obstacles were, why it was difficult for Sir Humphrey Davy to prepare it in quantities by this method, and having found out the difficulties, he quickly devised a method for overcoming them and shortly had an electric process for preparing sodium running in beautiful simplicity.

I had the pleasure of going with Mr. Castner through his works near Birmingham, England. There must have been forty or fifty at that time (there may have been a hundred since) of those little iron decomposing cells two feet deep and a foot in diameter, each one loaded with caustic soda, and with a current of electricity passing through it day and night. Every half hour the workmen came around, lifted the covers, and ladled out the metallic sodium, put it into air-tight cylinders, and sent it wherever it could be made use of.

The process went on day and night; there was no need of stopping it. From time to time additional caustic soda was poured in, and the whole business was reduced to the greatest

simplicity. No process we have is more simple or runs more regularly without accident or interruption.

That is the record of Mr. Castner in sodium, and he certainly compares favorably with any chemist in the intelligence and acuteness with which he discovered the obstacles in the way of anything he wished to accomplish, and the cleverness with which he overcame those obstacles, and established on a firm basis each of the industries which interested him.

I might say in addition to the improvements already mentioned that Castner turned his attention to efforts to prepare cyanides in other ways, and that he invented several processes for the manufacture of cyanides and received patents for them.

While Mr. Castner's attention was thus directed to sodium, it occurred to him that he might also devise a process for making caustic soda. Caustic soda had always been made from the carbonate, which was made from salt by a complicated chemical process. A great many efforts had been made to manufacture it by electricity. I presume a hundred or more different plans had been suggested, and different forms of apparatus had been devised for accomplishing this purpose.

Common salt consists of sodium and chlorine, and if the electric current is passed through the salt, it tears the sodium and chlorine apart. If it is in a melted state the chlorine escapes from one electrode and the metallic sodium escapes by way of the other electrode. The greatest difficulties, however, were experienced, and the processes were impractical.

Most inventors have contented themselves with decomposing the common salt while dissolved in water, but the difficulties encountered in this were numerous and almost insurmountable. The sodium liberated decomposes the water and forms caustic soda, so caustic soda and chlorine are in the same solution, but they at once get together again and produce hypochlorites, chlorates, etc., which attack the electrodes and make the process a complete failure. Chemist after chemist had modified the process, but not one made it a complete success. It was thought that perhaps some kind of a diaphragm between the electrodes to prevent the products from mingling would produce a good result. But immediately the diaphragm was employed, it became an obstruction and interfered with the passage of the current. Another great difficulty was due to the fact that caustic soda was always

produced in the solution of salt and consequently it was not pure. The product, under the most favorable circumstances, would be a mixture of caustic soda and salt. So although there were numerous patents issued, not one was a success.

Mr. Castner invented the first process which could be said to be a complete success, for accomplishing what French, German, English and American chemists had been at work for a hundred years.

The object is to prevent the sodium at the negative electrode from coming in contact with the chlorine at the positive electrode, and also to prevent the metallic sodium from being acted upon by the water present. Now, Castner had a beautiful method of accomplishing this. His method was to put metallic mercury at the bottom of his vessel and make it the negative electrode; then the sodium as fast as it is liberated by the current is taken up by the metallic mercury and protected in that way both from the action of water and chlorine. The chlorine is led away to proper chambers where it is used for the manufacture of bleaching powder.

Now that was only the beginning of the invention. If that had been all the process would never have been a success. Others had thought of that, but their inventions were always failures because they had not gone further.

Castner said, in order to make a success I must get the metallic mercury out of the vessel as soon as possible and into another vessel where by pure water I can extract the sodium and thus prepare pure caustic soda. The matter worked out in the simplest way. He made a vessel with two cells with a partition between, but that partition extends down into a groove in the bottom of the cell, so it does not touch the sides or bottom but leaves a passage between the two compartments always filled with mercury.

Say the left hand cell is the decomposing cell, in that are the anodes, and the mercury cathode lays on the bottom, fills the groove under the partition, and rises up into the other cell and covers the bottom of that. In this other cell is placed an electrode, and, to begin with, a little solution of caustic soda, which is a good conductor of electricity. Now, under one end of the cells is an eccentric cam, which rotates about once a minute, so that once a minute the cell is tilted just enough to cause the metallic mercury to pass from one cell to the other through the groove under the partition. And to make it more satisfactory, he provides two de-

composing cells, the two outside cells, and a third cell in the center which is the one in which the sodium is converted into caustic soda. As the cells tip once a minute, the tipping carries the mercury into the middle cell where the electric current attacks it and makes the caustic soda, first from one side, then from the other. So the operation goes on year in and year out. It is only necessary to keep up the supply of salt solution and to run a stream of water into the middle cell where the sodium is taken out of the mercury and the caustic soda is formed.

At the Niagara Falls establishment, where there are 540 of these triple cells, the work goes on without intermission. If a visitor looks into the works there does not seem to be anything going on; yet there are trains of cars carrying away great iron tanks filled with caustic soda which was run out of these cells, and great casks of bleaching powder formed in the chlorine chambers.

During the last year works were erected to increase the output four-fold, to carry out this process of making caustic soda.

The chlorine is carried off into chambers and used in the manufacture of bleaching powder. This is the first time in the history of this country that we have been able to manufacture bleaching powder. We have never before been able to produce bleaching powder at a price which would enable us to compete with the manufacturers of England and the Continent.

There are numerous inventions in connection with these which I might say a word about. For instance, great difficulties were experienced in all electrolytic methods caused by the destruction which quickly overtakes the anodes, caused by the liberation of chlorine in the solution of common salt and in the presence of water. The anode disintegrates, and this disintegration is one of the most serious difficulties encountered by the chemists.

It occurred to Mr. Castner to obviate this difficulty by converting these anodes into graphite, and he found by experiment that after the carbon anodes are properly shaped it is only necessary to put them into the electric furnace and expose them to the action of a powerful electric current. They are made out of coke, but after the electric heating they become graphite, and this graphite resists the disintegrating action of the solutions.

With regard to the practical application of these inventions, I may say that the manufacture of sodium is carried out at Niagara Falls on a large scale, as well as all the other products made from

it, such as peroxide of sodium, cyanide of sodium and cyanide of potassium. It is also practiced abroad at Runcorn, near Liverpool, under the patents of Mr. Castner, and also in Germany.

I have reason to believe that it is also practiced in some other places without the use of his patents, that is, surreptitiously. I tried to gratify my curiosity when last in Switzerland by visiting one of these manufactories, but was refused admittance, but I heard the snapping of the little explosions of oxygen and hydrogen so characteristic of Castner's sodium process. The hydrogen is liberated and when it comes in contact with the oxygen a snapping sound occurs, due to explosions, which is so characteristic to anyone who had seen that process that he cannot fail to recognize it.

The caustic soda process is carried on at Niagara Falls on a very large scale, and at Runcorn.

I have endeavored in these few words to give you an idea of the results of Mr. Castner's wonderful inventive genius. Whatever he took hold of, whatever he turned his attention to, he left in much better position than he found it. He never worked on a chemical process that he did not invent a better one to accomplish the same result, and I consider him one of our most distinguished chemical students, am proud that he was a pupil in the School of Mines, and am glad his profile and his name will remain forever on the walls of Columbia University, to show our young men what he has accomplished.

Mr. Castner was of a most agreeable disposition, sweet and lovable in all his ways; honorable to the highest degree. I have never known a man for whom I had higher respect or greater affection.

I take pleasure in introducing Dr. Marcus Benjamin, a classmate of Mr. Castner's in the School of Mines from 1875 to 1878.

Address of Dr. Marcus Benjamin.

Among the many enthusiastic students of chemistry under Wöhler, the discoverer of aluminium, was the distinguished scientist, who from its inception has been head of the chemical department of our School of Mines. This fact is of special interest on this occasion for we meet to do honor to the memory of one whose name must always be associated with that of Wöhler, and Chandler is the connecting link between the two. May I add that in 1862 Chandler made his announcement of the discovery of a new ele-

ment in the platinum sands of Oregon, and of all those who are proud to have studied under him at Columbia, Iles and Castner alone have achieved eminence in the application of chemistry to the purification of metals.

It is, however, concerning the personality of my friend that I am to address you more particularly this afternoon.

Hamilton Young Castner, the second son of Samuel and Julia A. Castner, was born in Brooklyn, N. Y., on September 11, 1858. After preliminary studies at the Brooklyn Polytechnic Institute he entered the School of Mines in the autumn of 1875 with the class of '79. During the first year he manifested considerable interest in boating, and pulled bow on the first freshman crew that Columbia ever sent to an intercollegiate regatta. He served as coxswain to the four-oared crew that won in the Harlem regatta in June, 1877, and also acted in a similar capacity to the eight that yielded to Harvard at Springfield a few days later. The college annals show that he was a member of the Psi Upsilon fraternity, and of the Junior Society in the School of Mines.

On his return to Columbia in the autumn of 1876 he abandoned the regular course of studies and thereafter devoted exclusive attention to chemistry and allied subjects, making a specialty of analytical chemistry. After completing the course of qualitative analysis he entered the Quantitative Laboratory and was assigned to a table near my own. Our acquaintance soon developed into friendship, which then continued until his death. His earnest devotion to work and conscientious efforts to succeed, are pleasantly remembered as conspicuous traits of his character at that time. His perseverance in face of difficulties and a determination to accomplish the desired results even then manifested themselves.

Unlike many of us, the easiest way never appealed to him — his ambition was always to find the best way. As illustrating this phase of character I remember very well the following experience: The college term had closed and all regular work was over. I had wandered down to the office of the Dean to learn the results of an examination and found Castner with a wagon and load of bottles. On asking for an explanation, I learned that he was about to collect samples of water from all of the wells then in existence in New York. As he was not an applicant for a degree I argued with him that this work was an absolute waste of time, but he persisted, and it is gratifying to add that the Board of Health, of

which Dr. Chandler was then President, soon ordered all wells used as a source for drinking water to be closed up. Undoubtedly it was Castner's results that led to this action, and the health of the municipality improved in consequence of his devotion to duty.

Another bit of history from the past of our Alma Mater is suggested by the fact that these analyses were made in the laboratory of the old department of chemistry of Columbia College. It was to that department in 1857 — the year that Columbia moved to the site on Madison Avenue — that Joy was called to Columbia, and the first lectures in chemistry that Castner attended were delivered in that room.

His college course completed, Castner entered upon the active practice of his profession as an analytical and consulting chemist, opening a laboratory in Pine Street a few doors west of William, in the autumn of 1879. His success was immediate, and in a very short time he gathered around him a valuable following that accepted his advice on all chemical matters without question. Our relations at that time were exceedingly intimate and I saw him every day. His principal work was analyses of fertilizers, and I well recollect the first analysis made by him. He had completed his work and corroborated his results, but fearful lest an error might have been made he sent a sample of the material to a chemist of high standing in the immediate vicinity, whose results, however, were not in accordance with Castner's figures. I was hastily summoned. What was to be done? We discussed the matter and finally reached the conclusion that his own analysis must stand. Either he was competent or incompetent, and if the latter, then the sooner he found it out the better. But he was not incompetent, and his results came exactly between those of the other chemists who analyzed the material and his first commercial success was gained. Thereafter that special customer trusted Castner completely. His business grew and larger quarters were soon necessary, and taking into partnership his elder brother, Mr. E. B. Castner, he moved to offices on the corner of Pearl Street and Maiden Lane, where for several years he continued in business, finally, however, disposing of it to Elliott, Mattison & Hopke, as the firm styled themselves, three graduates in the chemical course of the School of Mines in the Class of '80.

Meanwhile, however, his active mind sought for occupation in studying improvements on then existing chemical processes. One

of the first problems that he took up was a method for the continuous production of bone charcoal. This he successfully accomplished, but was unable to find a market for the process, owing to the depressed financial condition of the country at that time, and also from the fact that the larger firms engaged in that business consolidated and reduced the price below that on which his calculations were based.

Castner then began his immortal work on an improved process for the cheaper production of aluminium, and with his usual energy and ability devised a modification of great value of the long and tedious method then in existence, which has received commendation from leading chemists all over the world. Sir Frederick A. Abel, in his retiring address before the British Association in 1890, said: "The success which has culminated in the admirable Castner process constitutes one of the most interesting of recent illustrations of the progress made in technical chemistry, consequent upon the happy blending of chemical with mechanical science, through the labors of the chemical engineer."

The care with which Castner investigated every step in the development of his invention may perhaps be illustrated by my own relations with him at that time. The files of Wagner's Jahresberichte, and the proceedings of the London, Paris, and Berlin chemical societies were thoroughly examined by me for every reference to any matter pertaining to his invention, and briefs of each mention found were made and submitted to him. These were then carefully considered and discussed from every point of view for the purpose of gaining some information that would improve his process.

Having successfully accomplished his result and thoroughly protected his invention by letters of patent, he sought for capital with which to erect works in this country, but this proving impossible he went to England and built an experimental plant in Oldbury.

Although deeply engrossed in his work he wrote me from time to time of his progress, and in appreciation of my interest sent me a number of shares of stock in the original company organized for the development of his invention. As the years went by our correspondence diminished and only once did I see him after he left for England, although on several occasions he sent me word of his being in New York. After my removal to Washington,

learning that he was spending the winter in Florida, I wrote and asked him to stop over in Washington and in return received a cordial reply. But the fatal illness that closed his career had already fastened its grip upon him and we never met again.

He died at Saranac Lake, New York, on October 11, 1899, a victim of tuberculosis, a disease that had previously carried away his father and two brothers.

The splendid success of his genius found its culmination in the extensive plant that bears his name at Niagara, and it was a glad moment when my colleagues on the Jury of Chemical Products, at the Pan-American Exposition in 1901, unanimously agreed with me in conferring the highest award possible on the Castner Company.

This silver metal and the white crystals, pure and beautiful, are the results of his many hours of study and research, and in the years to come they will ever preserve in the literature of chemistry the memory of him in whose honor this memorial has been erected by loving friends.

I now have the pleasure or introducing Dr. Joseph W. Richards, the Professor of Metallurgy at the Lehigh University.

Address of Dr. Joseph W. Richards.

I knew Mr. Hamilton Y. Castner for many years, and it gives me great gratification to come here to once more pay a tribute to his memory.

But one week before I received Dr. Chandler's invitation to be present on this occasion, I was asked by the editor of one of our prominent journals to write a biographical sketch of Mr. Hamilton Y. Castner, as one of the pioneers in electrical chemistry. It had been preceded by sketches of three other electro-chemists, and the propriety of publishing a sketch of Mr. Castner was so evident that the editor wished to add this sketch to those already published.

This pioneer work strikes the keynote of Mr. Castner's life work. We have a great respect for the pioneers who lay out the wilderness, and endure great hardships, and overcome all difficulties by perservance; but not one of them showed more manly and persevering and enduring qualities than Mr. Castner showed in following up his investigations and inventions. To any one attempting to investigate, to experiment and to develope a scientific process, the way of the experimenter is a hard and thorny one, and Mr. Castner stands out prominently in his success in this direction.

If a man makes two blades of grass grow where one only grew before, he is a benefactor of humanity. What shall we say, then, of a man who takes a raw material worth only a few dollars and extracts therefrom materials of the greatest value to mankind, worth hundreds of dollars.

Take the question of aluminium: Ten dollars' worth of raw material taken out of the ground would furnish, after Mr. Castner was through with it, one thousand dollars' worth of the metal.

Three and a half dollars' worth of common salt, after passing through his process, was converted into something like forty dollars' worth of caustic soda and fifty dollars' worth of bleaching powder.

The forty dollars' worth of caustic soda furnished, through his inventions, nearly one thousand dollars' worth of metallic sodium.

So we see the inestimable benefit to the race and our industrial progress that the efforts and works of such investigators bring about.

Personally my first acquaintance with Mr. Castner began with his taking up the aluminium industry. In 1887, going over to Runcorn, in England, he established large works for the manufacture of aluminium. The name of Runcorn has been spoken many times and is very familiar to me, because I was born there and my father had chemical works quite close, just across the canal from where Mr. Castner's chemical works were situated.

It is true inventors had worked for half a century in endeavors to cheapen the cost of aluminium and had been unsuccessful until Mr. Castner came along and by his process reduced the cost from eight dollars a pound to one dollar a pound. This work showed that he possessed the qualities and insight and pertinacity such as his predecessors had not possessed. He did not think of it accidentally, but his work was the culmination of a long series of experiments and investigations which tested all the manliness he had.

From the time Mr. Castner was in England we corresponded regularly, perhaps once a month, for several years, and the cost to which he finally reduced aluminium was in the neighborhood of eighty-five cents per pound. However, the invention of another process by which aluminium could be made at a cost of fifteen cents a pound rendered his process useless.

At Niagara Falls we have all been acquainted with the great power industries established there, where several millions of dollars

have been expended. Much of this power is used by the electro-chemical industries established at Niagara. Nearly one sixth of all the power generated there is utilized by the two industries founded by Mr. Castner.

As I passed there last week and saw the busy workmen working in the place, the long trains of cars which carried away the products, I thought what a lasting benefit! what a memorial this is. It speaks in tones as loud as any memorial on any tablet made. It is a living memorial to the work, the industry and the inventive abilities of this wonderful American.

Therefore I take great pleasure this afternoon in being present here to say these last few words of tribute to my friend who possessed not only the insight, the pertinacity, the courage, the mind of a great inventor, but also possessed what very few inventors do possess — the industrial spirit; the power not only to devise but to build; the power not only to invent, but to manage and erect. He was a leader of the industrial world as well as a leader in the inventive world — a combination so rare that but few of our great Americans possess it; and in that respect his abilities have always impressed themselves upon me as being a most unusual combination — the power of invention and the power of industrial application.

Mr. Castner's character was of the highest. His uprightness and integrity could not be better illustrated than in the splendid way in which he saved the Aluminium Company in England from financial bankruptcy. As Dr. Chandlar says, with the ground cut out from under his feet, he stood by that company, and by the power of his inventiveness and perseverance dragged that company out of commercial embarrassment and placed it on a safe footing. That is a most unparalleled example not only of inventive ability and industrial application, but of manly integrity; and in all these three ways his example is worthy to be perpetuated here among his friends, strangers and the students of Columbia University.

Woodbridge School,

FORMERLY

School of Mines Preparatory School.

---

417 Madison Avenue,

Between 48th and 49th Streets, NEW YORK CITY

Twenty-second Year Begins October 1st, 1904.

THE school is well equipped with physical and chemical laboratories, in which the students are required to perform a complete set of experiments illustrative of their recitations in physics and general chemistry. A special laboratory is devoted to qualitative chemical analysis for advanced students.

Five hundred Students of Columbia School of Mines have been instructed in the Woodbridge School. Also a large number have been prepared for Massachusetts Institute of Technology, Stevens Institute, Sheffield Scientific School, Lawrence Scientific School, Troy Polytechnic Institute, Cornell University, and the Classical, Medical, and Law Departments of Harvard, Yale, Columbia and Princeton.

A summer school for students who have failed in June begins August 13th and coaches men for the Fall examinations. All classes are limited to five. College men are coached in Freshman and Sophomore Mathematics and Quantitative Analysis.

An advanced course for older students prepares them to enter the second year class. Last June one of our students received his degree in Electrical Engineering in three years.

VOL. XXV. No. 3. APRIL, 1904.

THE SCHOOL OF MINES QUARTERLY.

A

JOURNAL OF APPLIED SCIENCE.

BOARD OF EDITORS.

A. J. MOSES, Prof. of Mineralogy.
J. F. KEMP, Prof. of Geology.
R. PEELE, Adj. Prof. of Mining.
R. E. MAYER, Adj. Prof. of Drawing.
E. WALLER, Analytical Chemist.
W. H. FREEDMAN, E E.,
T. H. HARRINGTON, Tutor in Drawing.

Managing Editor, R. E. MAYER,
Business Manager, T. H. HARRINGTON.

CONTENTS:

Notes on Quantitative Analysis for Mining Engineers, Part III. By Edmund H. Miller..... 221
The Detailed Design of a Railroad Bridge. By Wm. H. Burr, C. E. and Myron S. Falk, C. E..... 256
An Elementary Lecture on the Method of Least Squares. By Harold Jacoby..... 287
Aluminothermics. By Dr. Hans Goldschmidt..... 302
Abstracts—Analytical Chemistry. By E. Waller..... 327
Book Reviews..... 342

COLUMBIA UNIVERSITY
NEW YORK CITY.

Registered at the New York Post Office as Second Class Matter.

TWO DOLLARS PER YEAR. FIFTY CENTS PER NUMBER.
All Remittances should be made payable to Order of "The School of Mines Quarterly."

Portland Cement

THE LAWRENCE CEMENT CO.

ESTABLISHED 1832.

ERNEST R. ACKERMAN, President

This Company has manufactured and sold during 70 years upwards of **20,000,000** barrels of Cement; marketing the product in all the principal cities of the United States, Canada, West Indies, Philippines and South America.

The old Custom House on Wall Street, built in 1835–37, and the new Custom House on Bowling Green, now under construction, were built with cement sold by this Company.

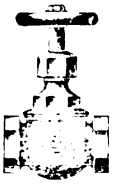
Used on the Old and on the New Stock Exchange in New York City, on the Brooklyn Bridge and New East River Bridge, and on the new Chamber of Commerce Building.

Detailed list of important Government Work Reservoir Dams, Sidewalks, Fortifications, Bridges, Municipal Buildings and Railroad Work where "DRAGON" has been used, furnished on application.

DRAGON PORTLAND CEMENT Stands the Highest Requirements of Architects, Engineers and Builders.

SALES OFFICES:

NEW YORK, No. 1 Broadway. 15th and Market Sts., PHILA.



SAID AN ENGINEER

"Yes, they did not know about valves at the time the plant was put in, but they do now. I am replacing all valves with the genuine ***Jenkins Bros.***"

BENJAMIN FRANKLIN SAID

"Experience keeps a dear school Remember this: they that will not be counseled cannot be helped"

Start your plant with ***Jenkins Bros. Valves*** and avoid trouble

JENKINS BROS., NEW YORK, BOSTON, PHILADELPHIA, CHICAGO, LONDON

THE

SCHOOL OF MINES QUARTERLY.

VOL. XXV. APRIL, 1904. No. 3.

NOTES ON QUANTITATIVE ANALYSIS FOR MINING ENGINEERS.—PART III.

BY EDMUND H. MILLER.

CHAPTER XIII.

The Determination of Antimony in Ores.

On account of the great inaccuracy of the fire assay for antimony it has been abandoned and its place taken by a "wet assay." Before describing these methods a short description of the gravimetric determination will be given and a few of the more important separations of antimony.

The important ores of antimony are stibnite Sb_2S_3, cervantite Sb_2O_4, produced by the oxidation of the sulphide, and mixtures of the two usually containing more sulphide than oxide. As stibnite is soluble in hydrochloric acid containing a few drops of nitric, and cervantite is practically insoluble, we have three classes of ores; first, the soluble, stibnite and also the rarer oxide, senarmontite, Sb_2O_3; second, the insoluble; third, the partially soluble. They will be discussed in this order. The following method is taken largely from an article by Brown, *Journal American Chemical Society*, 21, 780, 1899.

GRAVIMETRIC METHOD.

Soluble Ores. — One gram of the finely ground ore is placed in a small beaker, 25 c.c. of concentrated hydrochloric acid added, cov-

ered with a watch glass and boiled until the ore is apparently decomposed, which reduces the hydrochloric acid to about 15 c.c.; about 2 grams of tartaric acid are added and when dissolved 5 or 6 drops of concentrated nitric acid and the boiling continued for several minutes. The nitric acid causes a violent reaction, accompanied by a more complete decomposition of the ore. The solution is allowed to cool, diluted slightly, the residue filtered, and washed with water. The residue should be tested for antimony, unless the ore is known to be completely soluble. The filtrate is diluted to about 250 c.c. and the antimony is precipitated as sulphide by a stream of hydrogen sulphide, which is passed through for an hour. At the end the solution should be warmed to insure the conversion of any basic chloride (formed by the dilution) to sulphide; after standing for an hour to allow the precipitate to collect and settle, it is filtered and washed with hydrogen sulphide water. There may be present in the ore, arsenic and also lead and other metals of the fifth group; the latter will be evident from the dark color of the sulphide. If the sulphide is impure, warm it with a strong solution of ammonium sulphide $(NH_4)_2S$, until the sulphides of arsenic and antimony have dissolved, then filter. The residue is lead sulphide, etc.; in it the lead can be found by methods already given. It should be remembered here that copper sulphide is slightly soluble in ammonium sulphide, so if it is present sodium or potassium sulphide should be used.

If mercury should be present and no copper use ammonium sulphide as mercuric sulphide is readily soluble in the fixed alkali sulphides. Tin is not likely to be present; it would dissolve with the arsenic and antimony readily if stannic sulphide, with difficulty if stannous sulphide. The separation of antimony from tin presents considerable difficulty. See the standard works on quantitative analysis and for the most recent descriptions of Clarke's method, etc., Rossing, *Zeitschrift für Analytische Chemie*, 41, 1, 1902, and Henz, *Zeitschrift für anorganische Chemie*, 37, 1–58, 1903.

The separation of the fifth and sixth groups is also incomplete by the ordinary methods when there are present mercury, copper and antimony, as sometimes happens with tetrahedrite (fahlerz). For this separation see Pretzfeld, *J. Am. Chem. Soc.*, Feb., 1903.

To the filtrate containing the arsenic and antimony as sulphosalts, dilute hydrochloric acid is added in slight excess, then the

solution is diluted to ensure complete separation of the antimony sulphide, which is soluble in even moderately strong hydrochloric acid, and the mixture of sulphides of arsenic and antimony and sulphur is filtered on balanced filters, washed with cold water and dried at 110° C. for two hours or more to constant weight. This gives the total weight of the mixture. It is removed from the paper, ground up and mixed in a small glass mortar and an exact weight, about 0.5 gram, is weighed off in a platinum or porcelain boat. This is placed in a piece of hard glass combustion tubing and the excess of sulphur, over that required to form Sb_2S_3 and the sulphide of arsenic, are driven off by heating in a current of carbon dioxide for 12–15 minutes. A steady stream of carbon dioxide should be passed through the tube to displace the air before the heating is begun, so as to prevent oxidation; the heating should be gradual and the final temperature about 250° C., considerably below a dull red heat.

From the weight of the residue of black antimonous sulphide, the total antimony in the mixture of sulphides and sulphur is calculated and so the antimony in the ore. Should it be impossible to carry out this method, which is the best, the mixture of sulphide, or a portion of it, can be converted to oxide, Sb_2O_4 by treating repeatedly with strong nitric acid. This method is not recommended as it is almost always attended by mechanical loss, but if nothing better can be done, carry it out as follows: Transfer as much as possible of the dried precipitate to a porcelain crucible, dissolve what adheres to the filter in freshly made ammonium sulphide, using as little as possible, and add the solution to the precipitate in the crucible; evaporate on a water-bath, add fuming nitric acid and allow to stand, carefully covered, for several hours; then add more nitric acid, evaporate again on a water-bath; next drive off the sulphuric acid formed and finally heat over a Bunsen burner (no blast), and weigh the Sb_2O_4. The arsenic will be volatilized.

Insoluble Ores. — One gram of the ore is mixed with 10 grams of flux, made up of equal parts of sodium carbonate and sulphur, in a porcelain crucible and covered by a layer of the same flux. The mixture is fused for about ten minutes, covered, in the muffle of an assay furnace or by a Bunsen burner. The heat should be low at first and gradually raised, but never high enough to volatilize antimony. The melt should be greenish; if it is yellow the

decomposition is probably incomplete unless there is scarcely any iron present. The melt is treated with hot water and the sulphides of iron, lead, etc. (those which do not form soluble sulphosalts), filtered out. In the filtrate the antimony is precipitated as sulphide by hydrochloric acid and the precipitate treated as just described.

This is Rose's method of decomposition and it is also efficacious for the breaking up of cassiterite. Partially soluble ores can be treated as insoluble or treated first like soluble ores and the residue fused.

Properties of Antimony Sulphide. — Insoluble in water and dilute acids; decomposed by concentrated nitric or sulphuric; soluble in concentrated hydrochloric; easily soluble in potassium or sodium hydroxide and alkali sulphides. Slightly soluble in ammonia and ammonium carbonate. The separation from arsenic by dissolving the sulphide of arsenic in ammonium carbonate is not quantitative. A better separation is Pattinson's. Obtain the arsenic and antimony in solution in the triad condition, add concentrated hydrochloric acid, so that the sp. gr. due to the acid shall exceed 1.17, and then precipitate the arsenic as sulphide. Arsenic sulphide is insoluble in concentrated hydrochloric acid, while in acid of 1.17 sp. gr. or over no antimony is precipitated.

Other methods of separating arsenic and antimony will be given under arsenic.

VOLUMETRIC METHODS.

WELLER'S METHOD.*

The ore is decomposed as already described and the antimony precipitated as sulphide, if arsenic is also present it must be separated. As tin does not interfere in this method Pattinson's separation can be used with stannous chloride to reduce the arsenic to arsenious chloride so that it will be promptly and completely separated as arsenious sulphide in the strong hydrochloric acid solution; then, after diluting the filtrate, the antimony is precipitated as sulphide, Sb_2S_3. Or the arsenic can be distilled off as arsenious chloride according to Fischer's distillation method (see next chapter).

The precipitated sulphide of antimony is dissolved in strong hydrochloric acid and is oxidized to the pentad condition by adding potassium or sodium chlorate in small portions and boiling till the

* Youtz, SCHOOL OF MINES QUARTERLY, July, 1903.

excess of chlorine is expelled and the oxides of chlorine driven out. It is essential that the oxidation shall be complete and all excess of oxidizing agent expelled, as the method depends on measuring the iodine liberated by the pentad antimony; using a standard thiosulphate solution, as with copper.

After oxidation the solution is boiled down to very nearly 50 c.c.; this is ascertained with sufficient accuracy by making a mark on the beaker; then 20 c.c. of concentrated hydrochloric acid are added and the solution diluted to 600–700 c.c. with recently boiled cold water. Then three grams of potassium iodide are added and after waiting a few minutes for the solution of the potassium iodide and the liberation of the iodine, the solution is titrated by sodium thiosulphate, using starch solution as indicator, till the blue color disappears. The end point is very sharp and satisfactory when these conditions are maintained exactly. It is very important that the amount of hydrochloric acid is kept constant; if too little is present basic iodides and chlorides of antimony separate out on dilution; if too much, the hydrochloric acid itself acts on the potassium iodide in the presence of air and liberates iodine. We obtain this constant quantity, no matter how much may be used in the solution of the sulphide, by boiling down to 50 c.c.; this will be acid of 20 per cent., the hydrochloric acid of constant boiling point. If it was weaker in the beginning, more water boils off, if stronger, more hydrochloric acid, until this strength of acid is reached. So by this means we obtain always the equivalent of 45 c.c. of concentrated hydrochloric acid in a volume of about 650 c.c.

The potassium iodide must be three grams, if more is used results which are too high are obtained. The liberation of iodine is not instantaneous so it is advisable to wait several minutes before titrating, otherwise the solution may be decolorized by the thiosulphate and then the blue color suddenly flashes back, because the reaction is not yet complete. When the end point is reached, under the right conditions, the decolorization lasts for several minutes.

The sodium thiosulphate solution used for the copper assay can be used here. Theoretically the standard against antimony would be obtained as follows: Copper standard: antimony standard:: atomic weight copper: one half atomic weight antimony. It has, however, been found that while the standards obtained from copper, from potassium dichromate and from iodine agree with each

other, that they do not agree, when calculated to antimony, with the results obtained by standardizing with pure antimony. The discrepancy is almost exactly one per cent., under the conditions for titration just given; so if the antimony standard is to be calculated from any of the others, one per cent. should be added to that standard. If the calculated standard is 0.0062 grams Sb the figure 0.006262 should be used under the conditions given, or if the ore contained by calculation 18 per cent. the percentage of antimony is 18.18. The true cause of this variation has not yet been explained but the same deviation has also been observed with arsenic. It is more satisfactory to restandardize against antimony if absolutely pure metallic antimony can be obtained. Weigh out about 0.2 gram and dissolve this in about 50 c.c. or more of concentrated hydrochloric acid with 1–2 c.c. of concentrated nitric acid, then complete the oxidation by adding portions of 0.5 gram of potassium or sodium chlorate, boil out the oxides of chlorine and proceed as described. No tartaric acid is used in this method.

The reaction may be indicated as follows:

$$Sb_2O_5 + 4HI = Sb_2O_3 + 2I_2 + 2H_2O.$$

The antimony after oxidation is probably present as antimonic acid and after reduction by hydriodic acid it is present partly as antimonious iodide and partly as antimonious chloride, depending on the relative mass of hydriodic and hydrochloric acids. As tin in the stannic condition is not reduced by hydriodic acid, antimony can be determined in the presence of tin. This is of importance in the analysis of alloys.

This method is not free from theoretical difficulties, but it is very rapid and gives excellent practical results when the proper conditions are maintained. The same thiosulphate solution can be used as for copper and the end point is sharp.

Mohr's Method.

This is exactly the reverse of Weller's method. The reactions can be indicated as follows:

Mohr ⟶ ⟵ Weller

$$Sb_2O_3 + 2I_2 + 2H_2O \rightleftharpoons Sb_2O_5 + 4HI.$$

In Mohr's method we prevent the reverse reaction by preventing any concentration of hydriodic acid by having an excess of alkali

present. In order not to decompose the starch or absorb iodine this excess of alkali must be bicarbonate, so the exact reaction becomes

$$Na_3SbO_3 + I_2 + 2NaHCO_3 = Na_3SbO_4 + 2NaI + H_2O + CO_2.$$

The same statement and a similar reaction applies also to arsenic so it is evident that no arsenic can be present.

When the antimony is in the pentad condition it must be reduced by heating with sulphurous acid. To the acid solution add 30 c.c. of sulphurous acid (about 5 per cent. SO_2) and boil till most of the sulphur dioxide is expelled, then add a second portion of 30 c.c. and boil out the sulphur dioxide completely, then add about two grams of tartaric acid, to prevent the subsequent precipitation of antimony as hydrated oxide and make the solution alkaline with sodium bicarbonate, add about 20 c.c. of a saturated solution in excess, cool and titrate with N/10 iodine, using starch as indicator, at a volume of about 200 c.c.

When the antimony is separated as sulphide, either Sb_2S_3 or Sb_2S_5, it is dissolved in hydrochloric acid. This, by the liberation of hydrogen sulphide, reduces the antimony to antimonious chloride, so that after adding tartaric acid and neutralizing the excess of acid by alkali, and then adding an excess of sodium bicarbonate it is ready for titration.

It is advisable to run a blank made by neutralizing the same amount of hydrochloric acid in the same way and adding the same excess of sodium bicarbonate, in order to see whether a small quantity of iodine is required when there is no antimony present. If this amounts to more than 0.1 c.c. it should be subtracted.

This method can be used for arsenic in exactly the same way, omitting the tartaric acid.

Conclusion. — Formerly antimony was weighed as sulphide, after washing with alcohol, to remove the water, then with carbon bisulphide to take out the free sulphur and drying at 250° C. The results are always high and the method is only to be used for very small quantities, under 1 per cent. A comparison of results has shown the weighing as oxide to be slightly low and that the Mohr and Weller methods give accurate results.

The application of the volumetric methods to insoluble ores containing both arsenic and antimony will be indicated in the next chapter.

CHAPTER XIV.

The Determination of Arsenic in Ores.

Distillation Method.

This method consists in distilling off the arsenic as arsenious chloride, and so affords a most perfect separation from antimony and tin. Although it requires considerable apparatus, it must be regarded as the standard method of separation; besides being applicable to ores it is even better for material containing only very low percentages of arsenic,—pig copper, etc. It was devised by Professor Emil Fischer, of Berlin.

Arsenic ores are almost always sulphides, they may be decomposed by the fusion methods given under antimony, and the arsenic precipitated as sulphide. The original ore, or the sixth-group sulphides, are treated as follows: Place about two grams of potassium chlorate on the bottom of a beaker; on this place the weighed sample of ore, from 0.5 to 3 grams, depending on the richness, or the precipitated sulphides; then about a gram more of potassium or sodium chlorate, sufficient to cover the ore; pour in cautiously little by little a mixture of 30 c.c. of concentrated hydrochloric acid and 10 c.c. of water, cover the beaker and heat on a water-bath till the decomposition is complete and the oxides of chlorine, etc., driven off so as not to use up the ferrous salt added later. It is very important that the oxidation is complete to H_3AsO_4, as the arsenious chloride would be lost by boiling. If antimony is also to be determined, filter off any residue on asbestos, transfer the solution to a distilling flask (about 400 c.c.) using concentrated hydrochloric acid to rinse out the beaker, etc., add 5 to 20 grams of ferrous sulphate, depending on the quantity of arsenic present and make the solution up to about 200 c.c. in volume with concentrated hydrochloric acid. Connect the flask with a short condenser and under the end place an Erlenmeyer flask, about 250 c.c., containing a little water so as to cover the end of the condenser tube. Heat the flask on an asbestos pad by a burner; the arsenic acid is promptly reduced by the large excess of ferrous salt and forms arsenious chloride; this with hydrochloric acid begins to distill over before a temperature of 100° C. is reached. They are

condensed and collect in the Erlenmeyer flask. If this becomes very hot it should be surrounded by ice water. The apparatus should be set up in a place free from draughts so as to avoid back pressure. The distillation is continued until about half the original volume remains. Remove the Erlenmeyer flask and then the burner, when cool add another 100 c.c. of concentrated hydrochloric acid and repeat the distillation, catching the distillate as before. This is continued till no more arsenic distills over, which can easily be ascertained by testing a portion of the last distillate with hydrogen sulphide. Unless there is a very large quantity of arsenic present two or at most three distillations are all that are required. The solution in the flask must not be allowed to become too small or in other words the boiling point must not be allowed to rise above 107° C. for the temperature of the vapor and 112° C. for the solution; above this point antimony will begin to distill over. The distillation can be hastened by connecting the distilling flask with a second flask containing concentrated hydrochloric acid, this is heated so that a stream of hydrochloric acid gas passes in constantly, so that the strength of the acid is maintained and the removal of the arsenious chloride facilitated (like distilling with steam).

When the separation is complete, the apparatus is allowed to cool and the antimony from the distilling flask is precipitated by hydrogen sulphide after diluting largely and the antimony sulphide treated as already described. The arsenic is all in the distillate in the arsenious condition; it can be determined by nearly neutralizing the large excess of acid by soda, then adding a strong solution of sodium bicarbonate and titrating by $N/10$ iodine, exactly as given under antimony.

If a gravimetric method is to be used the arsenic is precipitated by hydrogen sulphide after diluting somewhat. Under these conditions the arsenic precipitates immediately as arsenious sulphide with very little sulphur, as it is entirely in the triad condition. If the amount is small it can be filtered on a Gooch crucible, washed with alcohol, then with carbon bisulphide and after drying at 110° C. weighed as sulphide. The results are slightly high. If the amount of arsenic is considerable, over 20 per cent., the error will increase proportionally and the arsenic must be dissolved, oxidized and finally weighed as magnesium pyroarsenate. The sulphide is dissolved in fuming nitric acid, the excess of acid and

oxides of nitrogen removed by boiling (for manipulation compare antimony sulphide when paper is used); or dissolve from the Gooch crucible by ammonia, evaporate down on a water-bath and then oxidize, or dissolve through by a small quantity of sodium hydroxide and oxidize by boiling with bromine.

Precipitation of Magnesium Ammonium Arsenate.

The conditions for the precipitation of magnesium ammonium arsenate are similar to those for magnesium ammoniun phosphate, but as the precipitate is more soluble and also more easily decomposed on ignition greater care must be used. When the arsenic is all in the pentad condition neutralize the acid solution with ammonia and add a slight excess. The volume should not exceed 100 c.c.; add magnesia mixture slowly, drop by drop, till in considerable excess, then alcohol equal to one third the volume of the solution and allow to stand in the cold over night. Filter on asbestos in a Gooch crucible and wash with 2½ per cent. ammonia containing a little alcohol, then with 20 per cent. alcohol alone, dry and ignite very gently to constant weight; weigh the $Mg_2As_2O_7$.

Separations of Arsenic and Antimony.

The action of hydrogen sulphide on arsenic and antimony is important but confusing.

The following separations are used:

Bunsen's Method. — When hydrogen sulphide is passed into an acid solution containing pentad arsenic and pentad antimony at the room temperature and then the hydrogen sulphide driven out by a current of air, antimonic sulphide, Sb_2S_5, only is precipitated. The hydrogen sulphide reduces the arsenic slowly, and if the excess is promptly driven out when the precipitation is complete, a satisfactory separation is effected.

Pattinson's Method. — In the separation described under antimony the hydrochloric acid was so strong that no antimony sulphide could form; here to get a prompt precipitation of arsenic it should be reduced before passing in hydrogen sulphide. When stannous chloride is used care must be taken to avoid an excess, which would precipitate metallic arsenic.

Neher's Method.—The solution containing arsenic and antimony, completely oxidized, and at least two volumes of concentrated hydrochloric acid to one of solution (*i. e.*, 1.14 sp. gr.), is cooled to zero

and saturated by a rapid stream of hydrogen sulphide. The arsenic is completely precipitated as pentasulphide, As_2S_5. McCay obtains the same result by saturating the solution containing pentad arsenic in the cold with hydrogen sulphide and then heating in a closed bottle (under pressure) in a water-bath. The arsenic can be filtered on a Gooch crucible and weighed as pentasulphide, As_2S_5. These separations are in accord with the theory that in a hot solution hydrogen sulphide reduces the arsenic first and then precipitates it as As_2S_3 mixed with sulphur; at the ordinary temperature this reduction goes on slowly, at zero it is not perceptible. Also as the acid increases the amount of pentasulphide increases. The limit being Neher's method where at 0°C. and in a strongly acid solution the precipitation is entirely as As_2S_5. So under ordinary conditions we obtain various mixtures of As_2S_5, As_2S_3 and S, depending on the temperature and the acidity.

For information on the formation of sulphoxy acids of arsenic, which by breaking up give these sulphides, see McCay, *J. Amer. Chem. Soc.*, 24, 661, 1902. And for more information on the separation, see Treadwell's "Quantitative Analysis," pp. 150–154 (German edition). When arsenic is to be removed in the course of analysis with the fifth and sixth groups, it should be reduced by sulphurous acid and the excess expelled. This is accomplished readily under pressure by heating in a strong bottle in boiling water, wrapped up in a towel to prevent flying glass, in case of an explosion.

Volumetric Methods.

The most important determination of arsenic for mining engineers is in ores, where it is present from 1–10 per cent. and for this determination some modification of Pearce's method is usually employed. The method is not free from objections and gives low results on arsenopyrite. This method and one recently divised by Danziger and Buckhout* which is also applicable to arsenopyrite will be described.

Pearce's Method as modified by Bennet† is based on the following facts. Arsenic when fused with a mixture of potassium nitrate and sodium carbonate is completely oxidized and forms

* School of Mines Quarterly, April, 1903.

† *J. Amer. Chem. Soc.*, 21, p. 431, 1899.

sodium arsenate, Na_3AsO_4, which is soluble in water, while antimony forms a quite insoluble sodium metantimoniate which is left behind when the melt is leached with water, together with oxide of iron, insoluble carbonates, etc. The filtrate contains beside, Na_3AsO_4, Na_2SO_4, Na_2SiO_3, $Na_2Al_2O_4$ and an excess of Na_2CO_3; this is acidified and the carbon dioxide expelled; then neutralized exactly and the arsenic precipitated as silver arsenate, Ag_3AsO_4, by an aqueous solution of silver nitrate. It is this neutralization which has given trouble; in the original method it was effected by ammonia, but as the precipitate (Ag_3AsO_4) is readily soluble either in nitric acid or ammonia, it was essential to obtain exactly the neutral point. The second plan for neutralizing was proposed by Canby, the addition of a cream of zinc oxide; this method will give a sufficiently neutral solution if the zinc oxide is allowed to remain in contact with the solution over night. The latest suggestion is that of Bennet to use acetic acid and a sensitive indicator like phenolphthalein.

The precipitate of silver arsenate is filtered off and the silver in it determined by Volhard's thiocyanate titration using ferric alum as an indicator. The method is therefore an indirect titration of the arsenic, and for three atoms of silver found there must have been present from the ore, one atom of arsenic. So the arsenic value for the thiocyanate solution is obtained from the silver standard by using the proportion,— atomic weight silver to one third atomic weight arsenic.

Solutions Required. — Aqueous nitrate of silver, made by dissolving silver nitrate crystals in water. (The nitric acid solution used to test for chlorides will not do here.)

A ten per cent. solution of ferric sulphate or a saturated solution of iron ammonium alum as indicator; a solution of ammonium thiocyanate containing about 8 grams per liter. This is standardized by dissolving portions of pure silver, about 0.2 gram each in nitric acid, 1.16 sp. gr. diluting to about 100 c.c.; adding 5 c.c. of the indicator and titrating until a faint permanent reddish color is produced. The silver is precipitated as thiocyanate. The end point is the production of red ferric thiocyanate.

Both standards should be placed on the bottle as the solution may be used for the determination of silver in alloys, etc. This solution keeps well and therefore does not require frequent re-standardizing.

Flux.— Make up a sufficient quantity of flux containing two parts of potassium nitrate by weight, to one part of sodium carbonate.

Assay. — Place a layer of the flux on the bottom of a Russia iron crucible, mix the weighed portion of the ore, 0.25 to 1 gram, depending on the quantity of arsenic, with 8–10 times its weight of the flux and place this on top of the first layer; cover this with a layer of potassium nitrate. Porcelain crucibles may be used, but they usually break, owing to the contraction of the flux on cooling.

Heat the crucible very gently and gradually, holding the burner in the hand and allowing the flame to heat different parts of the crudible in turn. The heating requires attention or arsenic will be lost with a high-grade ore. There must be no odor or fumes of arsenic at this point. After the fusion has become quiet, the heating is continued for several minutes and the contents caused to rotate to ensure complete fusion and oxidation. Allow to cool and leach with hot water, filter and wash the residue very thoroughly with hot water; acidify with nitric acid and boil vigorously till all the carbon dioxide is expelled. If any precepitate, such as hydrated silica, forms here it may be filtered out, as it would interfere with the filtration of the silver arsenate, but not with the accuracy of the results. Allow the solution to cool completely; add a few drops of phenolphthaleine and then dilute sodium hydroxide solution (not ammonia or sodium carbonate on account of the indicator) till the solution turns pink, then acetic acid drop by drop till the color is discharged, stirring between each addition, so as to stop when there is but a drop of acetic acid in excess. Then, to the cold solution add a slight excess of aqueous silver nitrate, filter the brick-red silver arsenate and wash it with cold water till free from silver. As silver acetate is sparingly soluble, this must be completely washed out as well as the excess of nitrate. Dissolve the precipitate through the paper with dilute nitric acid into a clean beaker; dilute to about 100 c.c.; add 5 c.c. of the ferric indicator, and titrate as in standardizing.

Sodium Peroxide Method.

Sodium peroxide has been found to be an admirable reagent for the decomposition of arsenic ores; its action is the same as the mixture of potassium nitrate and sodium carbonate to form sodium arsenate, but it acts more rapidly and effectively in preventing loss

by volatilization with high-grade ores. After destroying the excess of peroxide and filtering off the residue, we have an alkaline solution containing sodium arsenate. There are at least three volumetric methods by which the arsenic can be determined: (1st) Indirectly as silver arsenate as just described, (2nd) by standard alkali. Acidify the alkaline solution with hydrochloric or nitric acid in slight excess, boil out carbon dioxide, then add methyl orange and titrate till the solution turns yellow, with a dilute solution of sodium hydroxide. This marks the neutralization of the excess of hydrochloric or nitric acid and of one hydrogen of the arsenic acid; we have now in solution NaH_2AsO_4; add a few drops of phenol phthaleine, and titrate to a pink color with a standard solution of sodium hydroxide. The amount of alkali used is that required to neutralize the second hydrogen. Hence for each molecule of sodium hydroxide used there is present one atom of arsenic. This method is only outlined as it is not as accurate as the others.

Third method: Measuring the arsenic present by the amount of iodine liberated, as in Weller's method for antimony. This gives accurate results when carried out as follows: About half a gram of arsenopyrite or more of an ore containing less arsenic is mixed with 10–15 grams of sodium peroxide and placed in a large nickel crucible, so that it is not more than one third full, with a cover of sodium peroxide on top. The crucible is heated slowly at first, until the mass is fused, then the temperature is raised to a strong red heat for a couple of minutes, the crucible is held by tongs in the flame and the contents caused to rotate.* Allow to cool and leach with about 100 c.c. of hot water, then boil for five minutes, till the excess of sodium peroxide is completely decomposed, filter and wash with hot water containing sodium carbonate. Acidify with hydrochloric acid, boil out the carbon dioxide and evaporate to about 75 c.c. When cold, add about 75 c.c. of concentrated hydrochloric acid and allow to cool again, then add 3 grams of potassium iodide and titrate the liberated iodine by a standard sodium thiosulphate solution, till only a faint straw color, due to free iodine, remains; finish the titration, using starch solution as a spot test on a white tile, till no blue color is produced. The starch does not give satisfactory results when added to the solution, on account of the great quantity of hydrochloric acid, which has to be present to effect the quantitative liberation

* This is necessary to obtain complete decomposition of the ore.

of iodine. Pink and violet colors are formed which give an uncertain end point. The spot test is not tiresome in this case because it is possible to judge the end within a few drops by the yellow color of the solution.

As in the case of the antimony titration, the results, using the standard calculated from iodine or potassium dichromate, are about 1 per cent. low. So that 1 per cent. of the arsenic present should be added to the results; or better, standardize against freshly resublimed arsenious oxide, As_4O_6, as follows: Weigh out portions of 0.2–0.25 gram of resublimed arsenious oxide into small beakers; add to each about 0.5 gram of potassium chlorate and about 20 c.c. of concentrated hydrochloric acid and boil till the oxidation of the arsenic is complete and all yellow color has disappeared from the solution; add water and concentrated hydrochloric acid so that the final bulk is 100–150 c.c. and consists of half concentrated hydrochloric acid and half water (20 per cent. actual HCl). Cool, add three grams of potassium iodide and titrate as in the ore. Calculate the arsenic standard from the number of c.c. used. This is another titration where the results are varied by changes in the conditions of titration; here the important points are the temperature, the acidity and the amount of potassium iodide. When uniform conditions are maintained in standardizing and in titrating the results are very exact.

It only remains to indicate a procedure for ores containing both arsenic and antimony. Decompose the ore with sodium peroxide, as given, leach, boil, filter and precipitate the antimony by Bunsen's method (page 112), filter out the antimonic sulphide and titrate the arsenic in the filtrate as just described. To obtain the antimony dissolve the residue from the fusion in hydrochloric acid, filter, precipitate the antimony in the filtrate by hydrogen sulphide; add this to the sulphide already obtained: dissolve and titrate by either of the methods given under antimony ore.

ADDITIONAL REFERENCES TO BOTH ARSENIC AND ANTIMONY.

Review of methods for antimony, *Z. für Analytische Chemie*, 38, p. 664, 1899; for arsenic; same, 39, pp. 654–670 and 699–720, 1900. Beck and Fisher, Separation and Estimation of Arsenic and Antimony in Ores, SCHOOL OF MINES QUARTERLY, 20, 372.

CHAPTER XV.

Slag Analysis.

Under the title of Slag Analysis, nearly the whole subject of analytical chemistry and assaying might be discussed, for a great majority of the elements, both common and rare, are to be found in slags. No such attempt will be made here; what follows is merely a description of the technical analysis of some of the most important types of slags. For a more detailed and complete discussion of the subject the reader is referred to an article by Dr. Joüet on the Analysis of Slags and Cinders, in the SCHOOL OF MINES QUARTERLY, Vol. XXII., Nos. 1 and 2.

If the sample of slag has been chilled suddenly, it can usually be decomposed by acids, if allowed to cool slowly, a fusion with mixed carbonates is required. The important points to be shown in a technical analysis are: The ratio of bases to silica, the ratio of R_2O_3 bases to those of the RO type, the quantity of valuable metal present in a slag, from copper smelting, copper, etc.

For convenience in treating this subject the following classification is made:

Iron Slags. — The slags from the blast furnace in the production of pig iron, though containing much less iron than those which follow. They contain roughly 40–50 per cent. silica, 15–20 per cent. alumina, etc., 30–40 per cent. lime, magnesia, etc., besides iron, manganese, alkalies, sulphur, phosphorus, etc. The slags from basic processes are often rich in phosphoric acid. For this determination see Bulletin 46, Division of Chemistry, U. S. Department of Agriculture or Wiley's Agricultural Analysis, Vol. II.

Manganese Slags. — The slags formed in the production of spiegel, lower in silica than the iron slags, but containing up to ten per cent. of manganese. The difficult points in their analysis are the decomposition and the separation of manganese from alumina.

Lead Slags. — Containing roughly silica 32 per cent., iron 28 per cent., lime, etc., 20 per cent., the remainder being lead, zinc, antimony, sulphur, etc.

Copper Slags. — Similar in composition to the lead slags, but usually without lead or zinc and containing about half a per cent. of copper.

These four groups of slags fall naturally into two divisions, the iron and manganese slags and the lead and copper slags.

A general scheme will be given for each of these divisions, followed by a few comments and special precautions and by some separate methods for the determination of particular constituents. The methods will not be given in detail as they have already been discussed in these notes.

Iron and Manganese Slags.

In this scheme (page 120) provision has been made for titanium, barium, zinc, nickel and cobalt and also for the removal of the higher groups, although they are not usually present. When these are omitted the analysis becomes quite similar to that of limestone. Phosphorus and sulphur must be determined in separate portions. See Iron Ore.

In manganese slags, the fusion with mixed carbonates will usually be required to get complete decomposition, using a liberal quantity of flux and a long fusion. In making the basic acetate separation, the excess of acetic acid must be very small in order to get complete precipitation of alumina and must be repeated to remove the manganese which is sure to come down under these conditions.

The determinations of greatest importance and in many cases all that is required, are silica, oxides of iron and alumina, lime and magnesia. When the slag is soluble and only approximate results are required the determinations can be made as follows: *

Portion for silica and oxides of iron and alumina. Weigh out half a gram of the sample, place this in a casserole, add about 20 c.c. of water and stir well, then 15–20 c.c. of strong hydrochloric acid, heat to boiling, while stirring to break up any lumps; then evaporate rapidly to dryness and bake, take up with hydrochloric acid and water, boil and filter, ignite and weigh the silica (impure). In the filtrate the alumina is precipitated, together with ferric hydroxide, by ammonia and ammonium chloride. This should be reprecipitated, to free it from lime and magnesia, then ignited and weighed as usual.

* See also Lord's "Notes on Metallurgical Analysis," p. 201 and seq.

GENERAL SCHEME FOR IRON AND MANGANESE SLAGS.

Dissolve 1 gram in HCl and a few drops of HNO_3 or fuse with $NaKCO_3$ and a little KNO_3 and then dissolve in HCl. Evaporate to dryness, after adding a few drops of H_2SO_4; dehydrate silica; take up with dilute HCl; boil; filter.

Residue.

SiO_2, TiO_2, $BaSO_4$, weigh: expel SiO_2 by HF and H_2SO_4; reweigh: fuse residue with Na_2CO_3; dissolve in HCl; dilute, filter out the $BaSO_4$ and add filtrate to main filtrate. From the weight of $BaSO_4$ the barium can be calculated.

Filtrate.

Saturate with H_2S, to remove 5th and 6th groups, including Pt from crucible, filter.

Precipitate.

Sulphides usually rejected. May be used for As, Sb, etc., if present.

Filtrate.

Oxidize the iron by HNO_3 or H_2O_2; neutralize with Na_2CO_3; add $NaC_2H_3O_2$ dilute and boil (basic acetate precipitation), filter and repeat the precipitation.

Precipitate.

Redissolve again in HCl and precipitate by ammonia. Ignite and weigh the Fe_2O_3, Al_2O_3, TiO_2 and P_2O_5.

Fuse with $KHSO_4$ dissolve, reduce and titrate the iron: calculate to Fe_2O_3 and obtain the Al_2O_3 by difference. The percentage of Al_2O_3 can be subsequently corrected for P_2O_5 and TiO_2 if present.

Filtrates.

Combine the filtrates from the two basic acetate precipitations and evaporate; if any $Al(ON)_3$ separates, add it to the ammonia precipitate. Add bromine and heat; filter.

Precipitate.

MnO_2xH_2O Dissolve and determine Mn as $Mn_2P_2O_7$ or by Volhard's method.

Filtrate.

Make the solution alkaline with ammonia and saturate with H_2S.

Precipitate.

ZnS, NiS, CoS. Treat with 1.02 Sp. Gr. HCl saturated with H_2S.

Residue.

NiS. CoS dissolve in aqua regia evap. to fumes with H_2SO_4 and determine electrolytically.

Solution.

$ZnCl_2$ Precipitate as $ZnNH_4PO_4$ or titrate by $K_4Fe(CN)_6$.

Filtrate.

Precipitate the calcium as oxalate.

Precipitate.

CaC_2O_4 weigh as CaO or as $CaSO_4$ or dissolve and titrate the $H_2C_2O_4$ by $KMnO_4$.

Filtrate.

Precipitate the Mg as $MgNH_4PO_4$ ignite and weigh as $Mg_2P_2O_7$.

Portion for lime and alumina. -Treat a gram as above, using more water and acid; evaporate to dryness and heat to dehydrate the gelatinous silica; add hydrochloric acid and water, boil, pour into a 500-c.c. flask, rinse out the casserole with more hydrochloric acid and water, adding this also to the flask; dilute to about 300 c.c., add ammonia in slight excess, dilute to the mark (500 c.c.), mix thoroughly; filter through a dry paper and determine lime and magnesia in an aliquot part (250 or 200 c.c.) by the usual methods.

Lime may be precipitated as oxalate in the filtrate from silica without removing iron and alumina; the filtrate is heated to boiling and a slight excess of ammonia is added, then an oxalic acid solution, more than enough to combine with the lime, then ammonia is added again and finally enough oxalic acid to redissolve any iron. The solution is heated to boiling and the calcium oxalate filtered and either weighed or titrated as usual. The object here is to get sufficient oxalic acid to prevent the precipitation of iron. The method is not accurate and is spoiled by the presence of manganese.

None of these short methods is applicable to manganese slags.

Lead and Copper Slags.

If silver is present it will be largely with the first residue of silica, lead sulphate, etc. In this case it should be leached with ammonia before removing the lead sulphate.

In the scheme given (page 122) the barium is likely to be low, as the barium sulphate is somewhat soluble in ammonium acetate and also on account of the final reprecipitation in the presence of hydrochloric and tartaric acids. When barium is absent and the antimony in the residue disregarded this portion of the analysis becomes very simple.

Similarly in the main filtrate, if the trace of lead which escapes precipitation as sulphate is disregarded and bismuth is absent the fifth-group sulphides may be dissolved and the copper titrated at once.

It is not advisable to employ the volumetric method for antimony here as the amount is small and difficult to dissolve from the sulphur thrown down with it.

In treating the filtrate for iron, ammonia may be used instead of the basic acetate if manganese is absent. The percentage of

General Scheme for Lead and Copper Slags.

Treat 1 gram of the finely ground slag in a casserole with water, concentrated hydrochloric acid and a few drops of nitric acid or else fuse and dissolve in hydrochloric acid; add sulphuric acid and evaporate to fumes, dilute and filter, wash well to remove calcium sulphate.

Residue.

SiO_2, $PbSO_4$, possibly $BaSO_4$ and Sb_2O_3; leach out the lead sulphate by hot ammonium acetate, using as little as possible, filter.

Residue.	*Filtrate.*
SiO_2, $BaSO_4$, Sb_2O_3; weigh: drive off the SiO_2 by HF and H_2SO_4; re-weigh and determine silica by loss. $BaSO_4$ and Sb_2O_4 remain; fuse with Na_2CO_3; take up with HCl and $H_2C_4H_4O_6$; filter.	Precipitate the lead as $PbSO_4$, filter and weigh. In the filtrate precipitate any antimony as sulphide and add this to the main ppt. of 5th and 6th group metals.

Precipitate.	*Filtrate.*
$BaSO_4$, weigh.	Precipitate the antimony by H_2S and add to main precipitate.

Filtrate.

Add about 1 c.c. of conc. HCl and saturate with H_2S.

Precipitate.	*Filtrate.*
CuS, Sb_2S_3, traces of PbS and possibly Bi_2S_3, digest hot with Na_2S solution.	Oxidize the iron. Precipitate iron and alumina as basic acetate, and proceed from this point according to the scheme given for iron and manganese slags.

Residue.	*Solution.*
CuS, PbS (traces), Bi_2S_3(?) Dissolve in HNO_3; evaporate to fumes to throw out lead as sulphate. Filtrate; separate the bismuth and then determine the copper either electrolytically or volumetrically.	Na_3SbS_3 etc. acidify, filter out the Sb_2S_5+S; weigh as Sb_2S_3 or as Sb_2O_4.

iron is usually high and no particular difficulties are likely to be met.

Sulphur is occasionally determined in lead slags. This is either done by the Fahlberg-Iles method* or as follows:† One gram of the slag is treated in a casserole with a few c.c. of water, 10 c.c. of concentrated nitric acid and finally 20–25 c.c. of concentrated hydrochloric acid; boiled for about ten minutes, more hydrochloric acid added, and then evaporated to dryness and baked on a hot plate. When cold it is taken up with concentrated hydrochloric acid and water and boiled thoroughly; then the free acid neutralized with ammonia and exactly six c.c. of concentrated hydrochloric acid added and the boiling and stirring continued till it is certain that all the iron oxide and lead sulphate are in solution; diluted to 200 c.c., 25 c.c. of 10 per cent. barium chloride added and the solution boiled for 15 to 20 minutes, filtered and washed. The precipitate is ignited in a platimum crucible, the silica driven off by hydrochloric and sulphuric acids and the barium sulphate weighed. If the slag is not chilled, it will not be decomposed thoroughly, so the barium sulphate will be impure. With soluble slags this method gives good results and is much shorter than the Fahlberg-Iles.

When the results are required in a very short time accuracy must give way to rapidity. So time is saved by working at once on a number of separate portions. (See Furman's "Manual on Assaying.")

The following methods are employed for these slags:

Silica. — Dissolve half a gram in water and hydrochloric acid, filter, ignite and weigh the silica (which is of course impure).

Barium. — Dissolve half a gram in hydrochloric acid, add sulphuric acid and evaporate to fumes, neutralize the excess of sulphuric acid by ammonia, add 6 c.c. of hydrochloric acid, dilute to 200 c.c., boil and filter, weigh the silica and barium sulphate.

Iron. — 1 gram is dissolved and the iron titrated by either the dichromate or the permanganate method.

Manganese. — 1 gram, using Volhard's method.

Zinc. — 1 gram by the ferrocyanide method.

---

* Iles, Decomposition and Analysis of Slags, SCHOOL OF MINES QUARTERLY, V., p. 357.

† Miller and Thompson, paper read at N. Y. Section American Chem. Soc., December 4, 1903.

Copper. — 1 gram or more by the colorimetric method.

Lead. — 1 gram or more by volumetric methods or a larger portion by fire assay.

Silver is usually determined by fire assay.

The other determinations have been indicated under the iron and manganese slags.

When ferrous iron is to be determined, Cooke's method, as given by Hillebrand, Bulletin 176, U. S. Geological Survey, p. 92, is to be used.

Objection can easily be made to these schemes; they are incomplete on one hand and too long for some purposes on the other; but they are given as representing as much as is likely to be required of the mining engineer and as affording plans which can be amplified, modified or shortened to meet special needs. If more complete schemes are desired, they are to be found in the article by Dr. Joüet already mentioned. As rocks and slags have much in common from an analytical standpoint, Dr. Hillebrand's bulletin on rock analysis will give much valuable information.

CHAPTER XVI.

Flue Gas Analysis.

Any engineer is almost certain to have charge of some kind of a power plant, usually one where the heat of combustion of coal is the source of power; in order to ascertain the efficiency at which the plant is run, he must know at least the analysis, better also, the calorific power, of the coal, and the composition of the flue gas and the ash — the results of combustion.

The examination of the ash is for unburned carbon and requires no additional description.* The determinations required in the flue gas are carbon dioxide, carbon monoxide, oxygen and nitrogen; the first two are of the greatest importance, as the higher the carbon dioxide and the lower the monoxide, the more efficient is the combustion. If this is obtained by the introduction of an excessive quantity of air, both the carbon dioxide and monoxide will be low.

All that is required of the engineer is a knowledge of how to determine these four important constituents, really only three for the nitrogen is determined by difference, in order to ascertain whether the fuel is being used economically. This is obtained more satisfactorily by a number of analyses at frequent intervals, each made with rapidity, than by one analysis made with all the precautions and corrections, on account of the variations in the composition of the gas due to additions of fresh fuel, changing of draughts, etc. Therefore no mention will be made here of the so-called "exact" gas analysis, where all the measurements are made over mercury and allowance made for changes in temperature, barometer, etc., except to refer the reader to Hempel's Gas Analysis, recently translated by Prof. Dennis. We need only consider the most simple application of "technical" gas analysis.

Gas analysis is a branch of volumetric analysis and the results are always expressed in percentage by volume. Now, as the variation of volume of all gases for temperature and pressure is the same, the percentage by volume at any given temperature and pressure will be the same as under the standard conditions, 0°C.

* See coal analysis.

and 760 mm. It is therefore only when some particular constituent is absorbed and afterwards determined gravimetrically or by titration, that it is necessary in the "technical" analysis to apply the corrections for temperature, pressure and tension of aqueous vapor. However, variations of temperature or of pressure must be most carefully guarded against while the analysis is in progress, as these would vitiate the results. Whenever possible, the analysis is conducted in a room of even temperature, preferably with a northern exposure. All measurements are made at the atmospheric pressure and over water which has been previously saturated with a gas similar to that under examination.

If the temperature remains constant the tension of aqueous vapor is also constant, and when the analysis is conducted rapidly the variations of the atmospheric pressure are not likely to affect the results seriously. So as these conditions are practically constant, the results expressed in percentage by volume will agree within an allowable error of say 0.1 per cent. of the results calculated to the standard conditions. Unless there is a sudden barometric change or by carelessness the gas becomes changed in temperature, the error is likely to be less than the inaccuracy in reading the volumes.

Saturating the water over which the gas is measured or kept, and also the reagents, with the gases present, which are not to be absorbed by this particular reagent, deserves special emphasis. All gases are soluble in water to some extent and as carbon dioxide is soluble to the extent of about one volume of the gas to one volume of water, the error due to this cause may be great. The saturation is easily accomplished by running through one or two analyses of the gas, after the apparatus has been filled with water, reagents, etc., before making the analysis, the results of which are to be used.

The Orsat apparatus is the most convenient for flue gas analysis, as it is compact and portable.* It is assumed in these notes that this form of apparatus is to be used.

Reagents.

Carbon dioxide is removed by a strong solution of potassium hydioxide, 500 grams of commercial caustic potash to a liter of

* A description of this apparatus can be found in the text-books given at the end of this chapter or in the circulars of the dealers in chemical apparatus.

water, each cubic centimeter of this reagent absorbs about 40 c.c. of carbon dioxide. This is the first reagent used with the flue gas.

Oxygen is absorbed by an alkaline pyrogallate solution, made by dissolving (as far as possible out of contact with the air) 5 grams of pyrogallol, $C_6H_3(OH)_3$, in 100 c.c. of the potassium hydroxide given above. Pyrogallol or, as it is frequently termed, pyrogallic acid, is a triatomic phenol, when dissolved in potassium hydroxide the three hydrogens of the hydroxyl groups are replaced by potassium atoms. When oxygen is absorbed no definite reaction takes place, but acetic acid, and brown humus-like substances are formed. The reagent will be quickly exhausted if exposed to the air; each c.c. absorbs about 2 c.c. of oxygen. This is the second reagent used in the flue gas analysis; it is evident that as it contains an enormous excess of caustic alkali it would, if used first, absorb carbon dioxide as well as oxygen.

Carbon monoxide is absorbed by a hydrochloric acid solution of cuprous chloride, which is made as follows:* Cover the bottom of a large wide-mouthed bottle with black oxide of copper, not necessarily pure, to a depth of about half an inch; fill nearly full with hydrochloric acid 1.1 sp. gr.; add about a hundred pieces of stout copper wire, cut in lengths of about six inches, so that they shall reach from the bottom to the top of the bottle; allow to stand, shaking occasionally, till the solution is colorless; then withdraw for use. The action is that the cupric oxide dissolves in the hydrochloric acid giving cupric chloride, this in turn dissolves copper from the wires forming cuprous chloride, the reagent desired.

The wires keep up the strength of the solution and reduce any cupric chloride formed by the air back to cuprous. The solution should be nearly colorless when used. The amount of carbon monoxide absorbed per c.c. is given variously by different authorities, but it is safe to assume that it will absorb an equal volume of carbon monoxide. The reaction is supposed to result in the formation of an unstable addition product, $Cu_2Cl_2.CO$. As there is usually only a few tenths of a per cent. of carbon monoxide in flue gas, this reagent will last for some time if protected from oxidation or if kept in contact with metallic copper. This is the third and last reagent used with flue gas.

* Gill, "Gas Analysis for Engineers," p. 34.

Sampling.

The sample should be taken as close as possible to the point where the flame ends and at the place in the flue of smallest cross-section, to prevent admixture of air and to get a sample of the gas which is really the result of the combustion in progress when the sample is obtained. Tubes are usually inserted in the wall of the chimney or other flue, which should penetrate to the center and contain asbestos to filter out dust, etc. They may be made of hard glass (combustion tubing), porcelain or metal depending on the temperature. Iron tubes are, however, obectionable as they become coated with oxide, which is reduced by the carbon monoxide in the gas with an increase in the amount of carbon dioxide.

The end of the tube is provided with a cork or rubber stopper through which passes a smaller glass tube, which is connected by a short rubber tube with the sample tube. Many convenient forms of apparatus for samples of gas can be had from the dealers, but all that is necessary is a large pipette, 200–250 c.c., provided with a short piece of rubber tubing at both ends and two clamps.

As the draught of the chimney must be overcome in taking the sample, some form of aspirator is needed. Water pumps are convenient when water pressure is at hand, but a simple and serviceable pump * can be made by reversing the valve of an ordinary large-sized bicycle pump.

The aspirator is attached to the sample tube and the flue gases drawn through for several minutes to displace the air which fills the tube and connections; then the ends of the sample tube are closed (by the clamps on the rubber tubes) and the sample is taken to the Orsat apparatus.

Analysis.

The Orsat apparatus consists essentially of three pipettes containing the reagents already described and a measuring tube graduated from 0 to 100 c.c. in tenths, provided with a levelling bottle, so that the pressure of the gas can be made equal to that of the atmosphere. The measuring tube and connections are filled with water by turning a stop-cock and raising the levelling bottle; then the tube containing the sample is connected by one end, while the other is placed under water, to prevent admixture of air when the sample of gas is removed; the connections are

* Devised by Irving Langmuir.

opened and by lowering the levelling bottle a little more than 100 c.c. of the flue gas is drawn into the measuring tube; the sample tube is then closed and disconnected and the excess of flue gas above 100 c.c. driven out by raising the levelling bottle so that the liquid in the measuring tube and in the bottle shall coincide with the 100-c.c. mark. Then the stop-cock is turned to prevent the escape of gas and the analysis is begun. The gas is run into the first pipette, containing potassium hydroxide. By raising the levelling bottle, the gas displaces the alkali solution, which passes into the rear portion of the pipette, displacing in turn air which expands a rubber bag. In this way the reagents are kept from contact with the atmosphere. In the pipettes are a number of glass rods; when the reagent is displaced these rods remain wet and so give a large surface for the absorption of carbon dioxide from the flue gas. After three minutes the gas is drawn back into the measuring tube, care being taken that the reagent comes back to exactly the point at which it stood before on the capillary tube connecting with the pipette; and the gas is remeasured at the atmospheric pressure. The decrease in volume gives the percentage of carbon dioxide. In order to ensure the complete absorption of any constituent it is well to run the gas over again into the pipette for three minutes and then back and take a second reading; if more than two treatments are required, the reagent is becoming exhausted and should be renewed. When the carbon dioxide has been completely removed, the gas is run into the second pipette, containing alkaline pyrogallate, and the oxygen removed in the same way. As this reagent is likely to become weakened in a very short time several treatments are often necessary. After the oxygen has been removed and the second decrease in volume noted, the gas is run over into the third pipette containing cuprous chloride, for the removal of carbon monoxide; then back and the final reading taken. The residual gas is considered nitrogen.

Great care should be taken when making the readings to have the level in the levelling bottle and the measuring tube the same, so that the gas is under exactly atmospheric pressure each time.

Results.

While it is not the province of analytical chemistry to discuss the results, it is to be expected that the carbon dioxide will be from 5–12 per cent., the carbon monoxide 0.0–0.4 per cent., the

oxygen together with the carbon dioxide should usually be between 20 and 21 per cent., and the remainder nitrogen.

While there is some variation in the percentage of oxygen in the air in different places, country and city, streets and parks, it is very slight, and 20.9 per cent. is very close to the correct percentage. Now if we burn carbon in air completely to carbon dioxide, as the volume of carbon dioxide is equal to the volume of oxygen used, according to Avogadro's law, the sum of the percentages of oxygen and carbon dioxide should equal that of the oxygen in the air, *i. e.*, 20.9 per cent. But it often happens in the analysis of flue gas that the sum of these two does not equal 20.9 per cent.; for if any carbon monoxide is produced we get two volumes of carbon monoxide for each volume of oxygen, hence the percentage of nitrogen is diminished; on the other hand if hydrocarbons such as methane, etc., are present, from bituminous coal, we get one volume of carbon dioxide from two volumes of oxygen, as the water condenses, and therefore an increase in the percentage of nitrogen over that in the air. (See also Calculations of Analytical Chemistry, Chapter VIII.)

For further information on flue gas analysis the reader is referred to Gills' "Gas and Fuel Analysis for Engineers"; Stillman's "Engineering Chemistry," and Blair's "Chemical Analysis of Iron." For a complete discussion of gas analysis see Hempel's "Gas Analysis" translated by Dennis, and Winkler's "Technical Gas Analysis," translated and enlarged by Lunge.

CHAPTER XVII.

References to Additional Analysis.

The last chapter concluded the descriptions of the analyses required of the mining engineers at Columbia University, but not all those frequently needed in practice; so this final chapter will contain references to recent reliable descriptions of a number of additional analyses which are often required of mining engineers, metallurgists or chemists.

The following abbreviations will be used:

Journal of the American Chemical Society, J. Am. C. S.

Transactions of the American Institute of Mining Engineers, T. A. I. M. E.

School of Mines Quarterly, S. of M. Qly.

Chemical News, C. N.

Zeitschrift für Analytische Chemie, Z. A. C.

Zeitschrift für Anorganische Chemie, Z. Anorg. C.

Zeitschrift für Angewandte Chemie, Z. Angew. C.

Journal of the Society of Chemical Industry, J. S. C. I.

Engineering and Mining Journal, E. & M. J.

Alkalimetry and Acidimetry.

SUTTON'S Volumetric Analysis, Eighth Edition.

MOHR'S Lehrbuch der Titrirmethoden, Seventh Edition. Revised by Classen.

JAMES AND RITCHEY. Analyses Required for an Electrolytic Alkali Works. J. Am. C. S., 24, 469, 1902.

Review of Alkali Determinations. Z. A. C., 37, 684, 1898.

NORTH AND LEE. On the Estimation of Alkaline Hydrate or Bicarbonate in the Presence of Monocarbonate. J. S. C. I., 21, 322, 1902.

RIEGLER. Zur Titerstellung sowie zur Bestimmung kaustischer und kohlensaure Alkalien. Z. A. C., 38, 250, 1899.

Review. Standardizing Acid and Alkali. Z. A. C., 40, 411, 1901.

MARSHALL. Preparation of Standard Solutions of Sulphuric Acid. J. S. C. I., 18, 5, 1899.

Alkalies in Feldspar, Rock or Slag.

See Hillebrand, Bulletin 176, U. S. Geological Survey

Alloys.

SACK. Bibliographie der Metalllegierungen. Z. Anorg. C., 35, 249, 1903.

Type Metals, Bearing Metals, Etc.

ANDREWS. On the Analysis of Alloys of Tin, Lead, Antimony and Arsenic. J. Am. C. S., 17, 869, 1895.

GARRIGUES. Alloys for Metal Bearings. J. Am. C. S., 19, 934, 1897.

WALTERS AND AFFELDER. Analysis of Bronzes and Bearing Metals. J. Am. C. S., 25, 632, 1903.

HERZ. Trennung von Antimon und Zinn mittels Oxalsaure. Z. Anorg. C., 37, 1, 1903.

Bronze, Brass, German Silver.

CAIRNS. Quantitative Analysis.

TREADWELL. Analytische Chemie, Vol. II. (now translated by Hall).

SMITH. Electrochemical Analysis.

RIBAN. Traité d'analyse chimique par l'electrolyse.

Bismuth.

RIEDERER. Volumetric Determination of Bismuth as Molybdate and its Separation from Copper. J. Am. C. S., XXV., 907, 1903.

WIMMENAUR. Electrolytic Estimation of Bismuth. Z. Anorg. C., 27, 1, 1901.

CLARK. Separation of Bismuth from Lead. J. S. C. I., 19, 26, 1900.

Bismuth in Pig Lead. Furman's Assaying, p. 163.

Boric Acid and Borax.

THADDEEFF. Bestimung der Borsaure als Borfluokalium. Z. A. C., 36, 568, 1897.

GLADDING. Boric Acid Determination. J. Am. C. S., 20, 288, 1898.

SARGENT. Determination of Boric Acid in Tourmaline. J. Am. C. S., 21, 859, 1899.

Cadmium.

BIEWEND. Ueber den Kadmium gehalt der Zinkerze. Berg und Huttenmännische Z., 61, 401.

MILLER AND PAGE. Quantitative Determination of Cadmium. S. of M. Quarterly, 22, 391, 1901.

Calorific Power of Fuel.

ATWATER AND SNELL. Description of a Bomb Calorimeter and Method of its Use. J. Am. C. S., 25, 659, 1903.

PARR. The Peroxide Calorimeter as Applied to European Coals and Petroleum. J. Am. C. S., 24, 167, 1902.

LUNGE. Ueber das verfahren von Parr zur Bestimmung des Heizwerthes von Brennstoffen. Z. Angew. C., 14, 793, 1901.

KENT. Calorific Value of American Coals. T. A. I. M. E., November, 1897.

PARR. Coal Calorimeter. J. Am. C. S., 22, 646, 1900.

NOYES, W. A. Determination of the Heating Effect of Coals. J. Am. C. S., 17, 843, 1895.

Cement.

STILLMAN'S Engineering Chemistry.

MEADE. Chemical and Physical Examination of Portland Cement, 1901.

CANDLOT. Ciments et Chaux Hydrauliques. 1898, Paris.

LUNGE. Chemische-Technische Untersuchungs Methoden. Vol. 1, pp. 599–677.

HILLEBRAND AND RICHARDSON. Report on Analysis of Materials for Portland Cement Industry. J. S. C. I., 21, 12, 1902.

HILLEBRAND. Critical Review of Certain Cement Analyses, etc. J. Am. C. S., 25, 1180, 1903.

Chlorates, Etc.

SUTTON. Volumetric Analysis, p. 186, etc.

Chromium.

CAIRNS. Quantitative Analysis.

BLAIR. Chemical Analysis of Iron.

MCKENNA. Complete Analysis of Chrome Ore. Proc. Eng. Soc. of Western Pa., 63, 180, 1897.

MAHON. Chromium in Steel. J. Am. C. S., 21, 1057, 1899.

Cobalt.

CLASSEN. Ausgewahlte Methoden, p 425.

Cyanide Solutions.

EISSLER. The Cyanide Process for the Extraction of Gold, and other books on Gold Metallurgy, Rose, etc.

GREEN. Testing Cyanide Solutions Containing Zinc. Institute of Mining and Metallurgy, October 17, 1901.

CHRISTY. Electromotive Force of Metals in Cyanide Solutions. T. A. I. M. E., 30, 864.

Review of Methods of Analysis. Z. A. C., 38, 792, 1899.

SHARWOOD. Notes on the Estimation of Cyanogen, etc. J. Am. C. S., 19, 400, 1897.

Copper.

FRESENIUS. Hampe's method. Quantitative Analysis, English Edition, 1900, page 405.

KELLER. On the Analysis of American Refined Copper. J. Am. C. S., 16, 785, 1894.

HOLLARD. Analysis of Commerical Copper by Electrolytic Methods. Bulletin Soc. Chimique, 23, 292, 1900.

ULKE. Copper Assaying and Analysis, Commercial Methods. E. and M. J., December 16, 1899.

Review of Methods. Z. A. C., 37, 120, 1898.

Fluorine.

JANNASCH. Praktische Leitfaden der Gewichts Analyse, p. 267.

STAHL. Analysis of Commercial Hydrofluoric Acid. J. Am. C. S., 18, 415.

Indicators.

SUTTON. Volumetric Analysis.

Review of Indicators, Z. A. C., 42, 304, 1903.

LUNGE. Bericht der Indikatoren-Kommission. Z. Angew. C., 16, 145, 1903.

GLASER. Ueber Indicatoren. Z. A. C., 41, 36, 1902; also 38, 273, 1899.

Lead. Refined Lead.

CAIRNS. Quantitative Analysis.

Review of Methods, Z. A. C., 42, 628, 1903.

Lithium.

JANNASCH. Gewichtsanalyse.

WALLER. Bei der Bestimmung des Lithiums. Z. A. C., 36, 513, 1897.

Mercury.

FURMAN. Manual of Assaying.

CHISM. Assay for Mercury. E. & M. J., 66, 86.

SMITH AND WALLACE. Electrolytic Estimation of Mercury. J. Am. C. S., 18, 169, 1896.

RISING AND LENHER. An Electrolytic Method for the Determination of Mercury in Cinnabar. J. Am. C. S., 18, 96, 1896.

PRETZFELD. Gravimetric Estimation of Mercury and its Separation from Arsenic, Antimony and Copper. J. Am. C. S., XXV., 198, 1903.

Molybdenum.

KOPP. Molybdenum in Steel. J. Am. C. S., 24, 186, 1902.

AUCHY. Molybdenum in Steel. J. Am. C. S., 24, 273, 1902.

Nickel.

SARGENT. Determination of Nickel in Nickel Steel. J. Am. C. S., 21, 854, 1899.

EDWARDS. Nickel Assay. New Caledonia. E. & M. J., May 28, 1898.

LANGMUIR. Nickel in Nickel Ores. J. Am. C. S., 22, 102, 1900.

HERZ. Nickel Sulphide, etc. Z. Anorg. C., 28, 342, 1901.

TAGGART. Electrolytic Precipitation of Nickel from Phosphate Solutions. J. Am. C. S., 25, 1039, 1903.

Oils.

GILL. Oil Analysis.

ALLEN. Commercial Organic Analysis, Vol. II.

LEWKOWITSCH. Chemical Analysis of Oils, Fats and Waxes.

Paint.

ELLIS. White Paint Analysis (Evanston, Ill.).

THOMPSON. Analysis of White Paint. J. S. C. I., 15, 432 and 791, 1896.

GNEHM. Unorganische Farbstoffe in Lunge's Chemisch-Technische Untersuchungs Methoden, Vol. II., pp. 765–804.

Phosphates, Etc.

WYATT. Phosphates of America.

CHATARD. Phosphate Chemistry as it Concerns the Miner. T. A. I. M. E., 21, 160.

GLADDING. Determination of Iron Oxide and Alumina in Phosphate Rock. J. Am. C. S., 18, 717 and 721, 1896.
Bulletins of U. S. Dept. of Agriculture.

Platinum Metals.

CLASSEN. Ausgewählte Methoden der Analytischen Chemie. Vol. 1, 1901.
LEIDIE AND QUENNESSEN. Estimation of Platinum and Iridium in Platinum Ores. C. N., 84, 216, 1901.
RICHARDS. Estimation of Platinum, Gold and Silver in Alloys. Analyst, 27, 266, 1902.
WILEY. Recovery of Waste Platinum Chloride. J. Am. C. S., 19, 258, 1897.

Separations.

In general see the works of Fresenius, Classen and Treadwell; for the halogens and alkaline earths see Jannasch's Gewichtsanalyse.

Sulphur in Pyrites.

LUNGE. On the Estimation of Sulphur in Pyrites. J. Am. C. S., 17, 181, 1895.
GLADDING. J. Am. C. S., 16, 403, 1894.

Tin.

Review on Tin, Antimony and Arsenic. Z. A. C., 38, 307–323, 1899.
WELLS. Analysis of Tin Ore. S. of M. Qly, 12, 295, 1891.
MILLER. Assay of Tin Ore. S. of M. Qly., 13, 369, 1892.

Thorium and Other "Hydroxide" Elements.

Treadwell's Analytical Chemistry and Classen's Ausgewählte Methoden.

Titanium.

Review of the Determination of Titanium. Z. A. C., 40, 799, 1901.
BASKERVILLE. On the Analysis of Titaniferous Iron Ores. J. S. C. I., 19, 419, 1900.
POPE. Investigation of Magnetic Iron Ores from Eastern Ontario. T. A. I. M. E., 29, 372, 1899.
BAIN. The Estimation of Titanium. J. Am. C. S., 25, 1073, 1903.

Tungsten.

BORNTRÄGER. Rasche Wolframprobe und Analyse von Wolframerzen, etc. Z. A. C., 39, 361, 1900.

Tungsten in Steel: Blair; McKenna, C. N., 67, 1900; Auchy, J. Am. C. S., 21, 239, 1899.

Uranium.

KERN. Quantitative Separation and Determination of Uranium. J. Am. C. S., 23, 685–726, 1901.

FRITCHLE. Analysis of Uranium and Vanadium Ores. E. & M. J., Nov. 10, 1900.

Water.

MASON. Examination of Water. 1901.

STILLMAN. Engineering Chemistry, pp. 42–97. 1900.

For those determinations, to which no references are given, see the standard text-books on quantitative analysis, among these: Classen's "Ausgewählte Methoden der Analytischen Chemie, 2 vols., 1901 and 1903, Treadwell's "Analytische Chemie," vol. 1, qualitative, vol. 2, quantitative, recently translated by Hall, and Fresenius' "Quantitative Chemical Analysis" translated by Groves (English), 1900, or by Cohn (American), 1903, are the best; and also Waller's abstracts on Analytical Chemistry which are to be found in the SCHOOL OF MINES QUARTERLY.

THE DETAILED DESIGN OF A RAILROAD BRIDGE.

By WM. H. BURR, C. E., AND MYRON S. FALK, C. E.

The design of iron and steel truss bridges must necessarily contain little that is new; but on the other hand, such rapid development has been made even in so ordinary a piece of engineering work as the design of a steel bridge that a full and systematic statement of it as at present practiced must be of distinct value. While, therefore, the following exposition of the design of a steel railroad truss bridge cannot be regarded as disclosing much that partakes of the nature of an investigation of a new subject, it will at least exhibit a systematic application of engineering science in an important field of engineering practice.

The design of the bridge will be based on the following data, which in engineering practice would be furnished by the railroad company for which the bridge is to be built.

Length of span between centers of end pins. Panel length, 29′ 2″, and number of panels, 12	350′	0″
Distance between centers of trusses	18′	0″
Distance between centers of stringers	7′	6″
The center height U_5L_5 is	63′	0″
The intermediate height U_3L_3 is	54′	0″
The end height U_1L_1	36′	0″

The form of truss is of the type known as the broken upper chord with subdivided panels, as is clearly shown on the stress sheet, Plate I. As specified by the railroad company all of the material of the bridge is to be of medium steel; all the rivets are to be $\frac{7}{8}$ inch, except that $\frac{3}{4}$-inch rivets may be used in the flanges of 12-inch channel posts, in horizontal struts at the middle of posts and in the overhead lateral or sway bracing. The structure is to be designed according to Cooper's specifications of 1896.

ART. 1. STRESSES IN THE STRUCTURE.

The stresses in the structure are caused by its own or dead weight and by the live or moving load. The dead load may be divided into two parts, the weight of the floor system consisting of rails, ties, track fastenings, stringers and floor beams, and the trusses and bracing. Excerpts from Cooper's specifications relating to these loadings are the following:

§ 23. All the structures shall be proportioned to carry the following loads:

1. The weight of metal in the structure.

2. A floor weighing 400 pounds per linear foot of track to consist of rails, ties and guard timbers only.

These two items, taken together, shall constitute the dead load.

*3. A "live load" on each track, supposed to be moving in either direction, consisting of 2 "consolidation" engines, coupled and followed by a train load, distributed as shown on diagram E 40 (or 100,000 pounds equally distributed on two pairs of driving wheels, spaced seven and a half feet, center to center).**

The maximum stresses due to all positions of either of the above "live loads" of the required class, and of the "dead load," shall be taken to proportion all parts of the structure.

§ 27. Variation in temperature, to the extent of 150° F., shall be provided for.

§ 28. When the structures are on curves, the additional effects due to the centrifugal force of trains shall be considered as live load. It will be assumed to act 5 feet above base of rail, and will be computed for a speed of $50 \times 2d$ miles per hour; d being the degree of curve.

§ 29. All parts shall be so designed that the stresses coming upon them can be accurately calculated.

§ 28 does not apply to the structure under consideration, and the requirements of § 27 may be fulfilled by placing one end of the bridge upon a nest of movable rollers.

Art. 2. Determination of Dead Load Stresses.

The weight per linear foot of the trusses, not including the floor system but including all the lateral and cross-bracing, may be approximately estimated by means of the following formula: $W = al$, where W is the weight per linear foot of both trusses and bracing in pounds, a is a numerical coefficient and l is the length of span in feet. In the bridge under consideration a may be taken as 7.75. The weight of the two trusses then becomes 2,700 pounds per linear foot, or 39,380 pounds per panel per truss. This weight

* This part of the specifications is usually employed in determining the maximum bending moments and shears in the floor system. In the example under consideration this alternative loading has been neglected.

must be equally divided between the upper and lower panel points. The specifications require the weight of track to be taken at 400 pounds per linear foot, while the remainder of the floor system may be assumed to weigh 500 pounds per linear foot; hence these loads become 5,830 and 7,290 pounds per panel per truss respectively. They act at the lower panel points.

The upper panel point loading is then 19,690 pounds but the lower panel point loading becomes 32,810 pounds.

The dead load stresses are easily determined by graphic methods

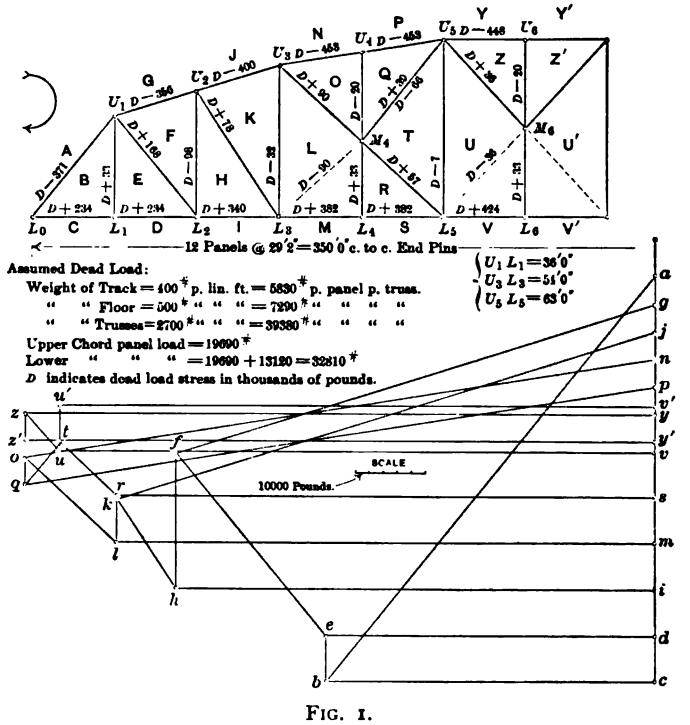

12 Panels @ 29′2″=350′0″c. to c. End Pins
Assumed Dead Load:
Weight of Track = 400 # p. lin. ft. = 5830 # p. panel p. truss.
" " Floor = 500 # " " " = 7290 # " " " "
" " Trusses = 2700 # " " " = 39380 # " " " "
Upper Chord panel load = 19690 #
Lower " " " = 19690 + 13120 = 32810 #
D indicates dead load stress in thousands of pounds.
U1 L1 = 36′0″
U3 L3 = 54′0″
U5 L5 = 63′0″
SCALE
10000 Pounds.

FIG. 1.

as shown in Fig. 1; for that figure only those web members shown in full lines are assumed to act, the dotted members acting as counters. It is unnecessary to explain the details of the figure; but to insure the accuracy of the graphic diagram it is important to check analytically the last stress found; the stress in L_5L_6 for instance is so found by passing a section through U_5U_6, U_5M_6 and L_5L_6 and taking the center at U_5.

The compression stresses in L_3M_4 and M_4U_5 are found by assum-

ing U_3M_4 not to exist and are quickly determined by the method of sections.

ART. 3. DETERMINATION OF LIVE LOAD STRESSES IN THE CHORDS.

The position of moving load for the greatest bending moment at any point in a truss or beam is found by the following familiar criterion, it being supposed for convenience that the train passes along the truss from right to left with W_1 as the front load:

$$\frac{l'}{l} = \frac{W_1 + W_2 + W_3 \cdots W_n'}{W_1 + W_2 + W_3 \cdots W_n}. \qquad (1)$$

In Eq. 1, l' represents the distance from the left end of the truss to the center of moments, *i. e.*, to the point in question, and l, the total length of the truss; $W_1 + W_2 \ldots W_n'$ the sum of the loads on l' and $W_1 + W_2 \ldots W_n$ the sum of the loads on l.

By the method of sections the stress in a chord member is found by dividing the maximum bending moment at the proper panel point by the normal distance (or lever arm) from the panel point to the chord member in question. This method is directly applicable to the truss cousidered, although a modification * is necessary in case of subdivided panels.

By drawing a reaction influence line both the truss reaction and the bending moment at any point for any position of the moving load may be at once measured; the diagram should be made on a large scale in order to attain the highest practicable degree of accuracy.

Number.	Wheel Load Number.	At Panel Point.	Stress in Pounds.	Remarks.
L_0L_1	5	L_1	+333,000	Train advancing from right to left.
L_1L_2	5	L_1	+333,000	"
L_2L_3	13	L_2	+480,000	"
L_3L_4	17	L_3	+537,000	"
L_4L_5	17	L_3	+537,000	"
L_5L_6	23	L_5	+590,000	"
L_0U_1	5	L_1	−528,000	"
U_1U_2	13	L_2	−502,000	"
U_2U_3	17	L_3	−562,000	"
U_3U_4	20	L_4	−631,000	Criterion of the subdivided panel.
U_4U_5	20	L_4	−631,000	
U_5U_6	26	L_6	−624,000	

* See paper "On the Use of Influence Lines in Graphic Statics," SCHOOL OF MINES QUARTERLY, July, 1903, p. 452.

By applying the criterion, Eq. 1, and completing these diagrams, the results shown in the preceding table will be obtained. The table exhibits both the positions of the concentrations for the greatest bending moments and the greatest stresses in the various chord members.

The uniform load is treated as a uniform series of loads of 25,000 pounds each; *i. e.*, load No. 23 in the table indicates the fifth load of this series.

ART. 4. DETERMINATION OF LIVE LOAD STRESSES IN WEB MEMBERS.

The graphic methods explained in the April, 1903, number of the SCHOOL OF MINES QUARTERLY were used to determine the position of the loading causing the maximum stresses in the web members of this truss, the modifications necessary for subdivided panels being given in the July number of the same publication.

The application of those methods gives all the results, both as to positions of loading and the greatest web stresses, exhibited in the following table:

Member.	Wheel Load Number	At Panel Point.	Stress in Pounds.	Remarks.
U_1L_2	4	L_2	+257,000	Train advancing from right to left.
U_2L_2	3	L_2	−161,000	"
U_2L_3	3	L_3	+160,000	"
U_3L_3	3	L_4	−103,000	"
U_3M_4	3	L_4, for panel L_3L_4	+204,000	"
M_4L_5	5	L_5, for panel L_3L_5	+168,000	"
U_5M_4	When L_4M_4 is maximum		+ 62,000	"
	3	L_3, for panel L_4L_5	+104,000	Train advancing from left to right.
M_4L_3	5	L_3, for panel L_3L_5	+ 82,000	"
U_5L_5	3	L_6	− 79,000	Train advancing from right to left.
U_5M_6	3	L_6, for panel L_5L_6	+173,000	"
M_6L_5	3	L_5, for panel L_5L_5	+136,000	"

The members U_1L_1, M_4L_4 and M_6L_6 are simply hangers. They carry in tension the maximum floor beam load, which occurs when wheel No. 5 is directly at the hanger.

The members U_4M_4 and U_6M_6 are simply supporting struts; they carry in compression the dead load assumed to exist at their upper ends, but they carry no live load.

The horizontal struts M_5M_4 and M_5M_6 are intended simply to prevent flexure of the long column into which they frame. They are subject to no direct stresses of either tension or compression

ART. 5. DETERMINATION OF WIND STRESSES.

Cooper's specifications prescribe:

"§ 24. *To provide for wind stresses and vibrations* * * * *the bottom lateral bracing in through bridges, for all spans up to 300 feet, shall be proportioned to resist a lateral force of 450 pounds for each foot of the span; 300 pounds of this to be treated as a moving load, and as acting on a train of cars, at a line 8.5 feet above base of rail.*

"* * * *the top lateral bracing in through bridges for all spans up to 300 feet shall be proportioned to resist a lateral force of 150 pounds for each foot of span.*

"*For spans exceeding 300 feet add in each of the above cases 10 pounds for each additional 30 feet of span.*

In accordance with these specifications, the assumed wind load for the bottom chord will be 470 pounds per lin. ft., and for the upper chord 170 pounds per lin. ft.

Upper Lateral Bracing.

The stresses for the upper chord lateral bracing are found in the most expeditious way by analytical methods.

The bracing may be considered a truss of 12 panels lying in a horizontal plane with its abutments at the feet of the end posts. The loading is fixed in position and equal to $29.1 \times 170 = 4{,}950$ pounds per panel, the reaction at the end post being 29.700 pounds. The secant of the angle of inclination between the web members and the perpendicular to the plane of the main truss is 1.9. The stresses in the web members are then found by multiplying the shear in the respective panels by this secant, and they are given on the stress sheet. It should be noted that in this treatment the panel of the portal is considered a part of the wind bracing, although the true lateral bracing in that panel is replaced by a portal frame. This involves no error in determining the

stresses of the webbing of the system, and is on the side of safety for the chord members. The stresses in the chord members are easily found by the method of sections.

Lower Lateral Bracing.

The lower lateral bracing is designed for a moving load of 300 pounds per lineal foot and a fixed load of 170 pounds per lineal foot. The stresses in the chord members of that system are easily found by multiplying the stresses in the chord members of the upper lateral system by the ratio between the loads of the two systems, *i. e.*, $\frac{470}{170} = 2.76$. The resulting stresses are shown on the stress sheet.

The stresses in the webbing are found by taking the stationary load the same as for the upper chord bracing and combining its effects with those due to the moving load. The following examples illustrate the method employed:

Web Member in Panel L_0L_1.

The stress in this member has its maximum value when the entire truss is covered by the moving load. The reaction then becomes 52,500 pounds, and the shear in the panel is $52,500 - (29.1 \times 300)/2 = 48,150$ pounds. The stress is then $48,150 \times 1.9 = 91,500$ pounds. To this must be added the stress due to the stationary wind load, viz., 5,100 pounds. The sum of these two quantities may then be assumed to be carried equally between the two intersecting web members within the panel, causing compression in the one and tension in the other member.

The resultant stress for each is therefore $\frac{1}{2}(91,500 + 51,000) = 71,250$ pounds.

Web Member in Panel L_1L_2.

For this member, $\frac{10}{11}$ of the bridge, or 318.1 feet, should be covered by the uniform moving load. The shear in the panel is then $43,400 - 3,620 = 39,780$ pounds, and the stress is 75,500 pounds. The stress due to the stationary load is 42,000 pounds; hence the final stress in the member is $\frac{1}{2}(75,500 + 42,000) = 58,750$ pounds.

The other web members of this lateral system are treated in precisely the same manner.

ART. 6. DESIGN OF LOWER CHORD MEMBERS.

The specifications which apply to the design of the lower chords are the following:

§ 30. All parts of the structures shall be proportioned in tension by the following allowed unit stresses:

Bottom chords, main diagonals, counters and long vertical (forged eye-bars)—for live loads 10,000 pounds per square inch and for dead loads 20,000 pounds per square inch.

§ 36. The stresses in the truss members or trestle posts from the assumed wind forces need not be considered except as follows:

1st. When the wind stresses on any member exceed one quarter of the maximum stresses due to the dead and live loads upon the same member. The section shall then be increased until the total stress per square inch will not exceed by more than one quarter the maximum fixed for dead and live loads only.

Member $L_5 - L_6$.

The stresses in this member, as taken from the stress sheet, are:

Dead load stress $= +$ 424,000 pounds.
Live load stress $= +$ 590,000 pounds.
Wind stress $= \pm$ 402,000 pounds.

Neglecting the wind stress, the area of cross-section required would be 80.2 sq. inches, as shown:

$$424{,}000 \div 20{,}000 = 21.2 \text{ sq. inches.}$$
$$590{,}000 \div 10.000 = 59.0 \text{ sq. inches.}$$
$$80.2 \text{ sq. inches.}$$

The actual intensity of stress in the member would then be $(424{,}000 + 590{,}000) \div 80.2 = 12{,}600$ pounds per sq. inch. The unit stress due to wind would then be

$$\frac{402{,}000}{80.2} = 5{,}010 \text{ pounds,}$$

which exceeds by $5{,}010 - 3{,}150 = 1{,}860$ pounds, one quarter of the unit stress due to the dead and live load. The sectional area of the chord member, therefore, must be increased until the intensity of stress does not exceed $12{,}600 \times \frac{5}{4} = 15{,}750$ pounds. The combined dead, live and wind loads is 1,416,000 pounds. Hence the required area of cross-section will be

$$\frac{1,416,000}{15,750} = 89.9 \text{ sq. inches.}$$

The member will then be composed of 6 eye bars, each 8 inches deep by 1⅞ inches thick, the area of whose combined cross-section will be 90 sq. inches.

Other lower chord members are treated in exactly the same way, and it will suffice to consider one more only.

Member $L_3 - L_4$.

Dead load stress = + 382,000 lbs. @ 20,000 lbs. = 19.1 sq. in.
Live load stress = + 537,000 lbs. @ 10,000 lbs. = 53.7 sq. in.
72.8 sq. in.

Wind stress = + 356,000 lbs.
Total stress = + 1,275,000 lbs.

Neglecting wind stress, the average stress in the member would be

$$\frac{382,000 + 537,000}{72.8} = 12,620 \text{ pounds per sq. inch.}$$

Adding 25 per cent. to this stress on account of wind, the final section required becomes

$$\frac{1,275,000}{(12,620 + 3,154)} = 80.8 \text{ sq. inches.}$$

The member will be composed of 6 eye-bars, each $8 \times 1\frac{11}{16}$ ins., whose combined area will be 81 sq. ins.

The lower chord members in the first two panels of the truss are subjected to a more sudden loading than those in the other panels; it is therefore customary to form these members either of shapes suitable to resist compression, such as channels, or stiffen them by latticing the eye-bars together. In the present case the latter plan will be adopted; the two center eye-bars, four being necessary, will be tied together by $2\frac{1}{2} \times \frac{1}{2}$ in. lattice bars.

Art. 7. Design of Upper Chord Members.

The following specifications apply to the design of the upper chord:

§ 33. *Compression members shall be proportioned by the following allowed unit stresses:*

Chord segments.

$$P = 10{,}000 - 45\frac{l}{r} \text{ for live load stresses.}$$

$$P = 20{,}000 - 90\frac{l}{r} \text{ for dead load stresses.}$$

End posts are not to be considered chord segments. All posts of through bridges:

$$P = 8{,}500 - 45\frac{l}{r} \text{ for live load stresses.}$$

$$P = 17{,}000 - 90\frac{l}{r} \text{ for dead load stresses,}$$

in which expressions P is the allowed stress in pounds per square inch of cross-section, l is the length of compression member in inches; r is the least radius of gyration of the section in inches.

No compression member, however, shall have a length exceeding 125 times its least radius of gyration.

§ 70. The unsupported width of plates subjected to compression shall not exceed 30 times their thickness, except cover plates of top chords and end posts, which will be limited to 40 times their thickness.

§ 90. In compression chord sections the material must mostly be concentrated at the sides, in the angles and vertical ribs. Not more than one plate, and this not exceeding ½ inch in thickness, shall be used as a cover plate, except when necessary to resist bending stresses or to comply with § 70.

Member U_5U_6.

Dead load stress = — 448,000 pounds.
Live load stress = — 624,000 pounds.

It will now simplify the design work to reduce the dead load stress to the equivalent live load stress; for this member the live load stress, plus one half the dead load stress, becomes 848,000 pounds.

The allowed unit stress is not a constant quality for compression members, but it depends upon the radius of gyration of the cross-section of the member. It becomes necessary, therefore, in designing, to assume some trial value for the radius of gyration. In the rectangular or box form of section adopted for upper chord members, it will usually be found that the radius of gyration has

a value of about 0.4 the depth of the side plates, the depth of the member being taken slightly greater than would be the case in a vertical column on account of the bending induced by its own weight. This depth is usually about one-twelfth to one-fifteenth the length.

In the case of U_5U_6, the depth of the member may be taken as 28 inches; the assumed radius of gyration becomes 11.2, and since l is 350 inches, the assumed unit stress becomes

$$P = 10{,}000 - 45\,\frac{350}{11.2} = 8{,}594 \text{ pounds per sq. inch.}$$

The approximate area required is therefore:

$$848{,}000 \div 8{,}594 = 98.7 \text{ sq. inches.}$$

A trial cross-section must now be formed from angles and plates of about this area, and tested to ascertain whether the assumed radius of gyration must be modified. The upper angles in the trial section should be made as light as possible, so that the cover plate may be largely balanced by the heavy bottom angles. Flat bars are frequently added to the horizontal legs of the lower angles for the same purpose. In this manner the center of gravity of the section may be brought down sufficiently near to mid depth

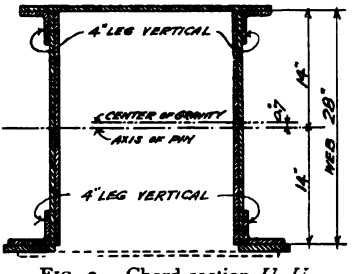


FIG. 2. Chord-section U_5-U_6.

to give the space needed inside the chord for the eye-bar heads, the pin axis being made to pass through the center of gravity of the section. At the same time there is gained the incidental but important advantage of an increased moment of inertia. If the chord were subject to no bending from its own weight, the axis of every pin should pass through the center of gravity of the section. It has been shown in Article 69,* that this flexure cannot be satisfactorily met and neutralized by the direct stress, particularly if

* Of Burr's "Course on Stresses in Bridges and Roof Trusses."

the chord is considered as continuous. It is best therefore to reduce the bending stresses by making the chord depth as great as possible and placing the axis of the pin either through the center of gravity of the section or but slightly below it.

Let the following section, Fig. 2, be tested:

		Sq. In.
1 cover plate	$30 \times \frac{5}{8}''$	$= 18.75$
2 L's	$4 \times 3\frac{1}{2} \times \frac{9}{16}''$	$= 7.80$
2 Webs	$28 \times \frac{1}{2}''$	$= 28.00$
2 "	$28 \times \frac{7}{16}''$	$= 24.50$
2 L's	$5 \times 4 \times \frac{9}{16}''$	$= 9.50$
2 bars	$6 \times \frac{7}{8}''$	$= 10.50$
		99.05

The position of the center of gravity of this section must first be determined by taking moments about the upper edge. The following calculation will determine its position.

Moment of cover plate	18.75×0.63	$= 11.8$
" " upper angles	7.80×1.91	$= 14.9$
" " web plates	52.50×14.63	$= 768.0$
" " lower angles	9.50×27.51	$= 261.8$
" " bars	10.50×29.07	$= 306.0$
	Total	$= 1,362.5$

Dividing this sum by the total area of the section determines the distance of the center of gravity from the upper edge, *i. e.*,

$$\frac{1362.5}{99.05} = 13.8 \text{ inches.}$$

The moment of inertia of the section must now be found about this center of gravity as an axis;

Cover plate,	$\frac{30 \times (.63)^3}{12} + [18.75 \times (13.5)^2] = 3,420.6$
Upper angles,	$2 \times 5.71 + [7.80 \times (11.9)^2] = 1,114.4$
Web plates,	$\frac{1.875 \times (28)^3}{12} + [52.50 \times (.8)^2] = 3,463.6$
Lower angles,	$2 \times 6.27 + [9.50 \times (13.7)^2] = 1,794.5$
Bars,	$\frac{12 \times (.875)^3}{12} + [10.50 \times (15.3)^2] = 2,460.7$
	Total $= 12,253.8$

The radius of gyration is equal to the square root of the quotient obtained by dividing the moment of inertia by the area, that is

$$r = \sqrt{\frac{I}{A}},$$

where $r =$ the radius of gyration of section,

$I =$ moment of inertia of section,

and $A =$ area of section.

In the present case

$$r = \sqrt{\frac{12253.8}{99.05}} = 11.1 \text{ inches.}$$

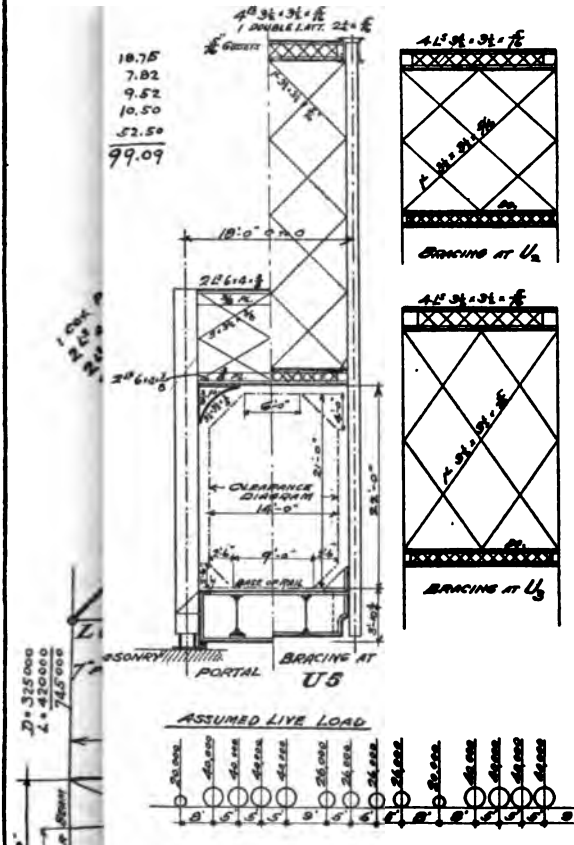
This is so nearly the value assumed that it will not be necessary to repeat the calculations with the true value of r. If there had been a considerable difference between the assumed and the actual values of r it would have been necessary to repeat the calculations with such changes in the trial section as would furnish satisfactorily correct results.

It must be determined whether the moment of inertia may not be smaller about the vertical axis of symmetry of the section; if this be the case, this smaller value of r must be used to determine the allowed intensity of stress. The calculations for this moment of inertia are as follows:

Cover plate,	$\frac{.625 \times (30)^3}{12}$	$= 1{,}405$
Upper angles,	$2[4.07 + (12.53)^2 \times 3.9]$	$= 1{,}236$
Web plates,	$2\left[\frac{(\frac{1}{16})^3 \times 28}{12} + 26.25 \times (11.03)^2\right]$	$= 6{,}404$
Lower angles,	$2[11.26 + (13.12)^2 \times 4.75]$	$= 1{,}656$
Bars,	$2\left[\frac{.875 \times (6)^3}{12} + 5.25 \times (13.5)^2\right]$	$= 1{,}944$
		$12{,}645$

This moment of inertia is larger than the one found for the horizontal axis, and it need not therefore be further considered.

The distance from back to back of the lower and upper angles will be made 28¼ inches, being slightly greater than the depth of side plates in order to prevent their interference with the cover plate or lower bars during manufacture. The axis of the pins will be placed 14½ inches from the upper edge of the cover plate, thus allowing a small counter moment from the direct stress due to a lever arm of 0.7 inch. The other upper chord members are treated in precisely the same manner. The stress sheet, Plate 1, shows in sufficient detail the forms of cross-section adopted.



MATERIAL MEDIUM STEEL RIVETS ⅞" EXCEPT THAT ¾" RIVETS MAY BE USED IN FLANGES OF 12" CHANNEL POSTS, IN HORIZONTAL STRUTS AT MIDDLE OF POSTS AND IN OVERHEAD SWAY BRACING.

STRINGERS WILL BE MILLED TO EXACT LENGTH AND STRINGER CONNECTIONS AND TOP CHORD FIELD SPLICES WILL BE REAMED TO AN IRON TEMPLATE.

WEBS OF PEDESTALS TO HAVE A BEARING ON SHOE PLATE.

\+ DENOTES TENSION
− " COMPRESSION
D - DEAD LOAD STRESSES
L - LIVE " "
W - WIND " "
I - IMPACT " "

PERMISSABLE STRESSES ACCORDING TO COOPER'S SPECIFICATIONS OF 1896.

TEN ACRE BRIDGE
OVER CONEMAUGH RIVER
ONE SINGLE TRACK THROUGH SPAN
350 FT. C TO C END PINS

STRESS SHEET

SCALE 1/16" = 1 FT.

End Post L_0U_1.

The end post is designed under a different provision of the specifications, the allowed intensity of stress for live load being found by the following formula:

$$p = 8{,}500 - 45\frac{l}{r}.$$

The length of the end post between pins is 558 inches, but it may be assumed that the effective length is only one half of this, since the post is supported at its center in one direction by an inclined strut, and in the direction at right angles by the portal bracing. Assuming $l = 279$ inches and $r = 11.1$ inches, the allowed intensity of stress becomes 7,370 pounds per square inch.

Dead load stress	$= -371{,}000$ pounds.
Live load stress	$= -528{,}000$ pounds.
(½ dead + live) load stress	$= 713{,}500$ pounds.

Therefore $\frac{713{,}500}{7{,}370} = 96.9$ square inches required.

The stress sheet indicates the section adopted for this member. It will be found on examination that the requirements of the specifications concerning the unsupported widths of plates in compression have been fulfilled.

ART. 8. DESIGN OF FLOOR BEAM HANGERS.

U_1L_1, L_4M_4, L_6M_6.

These members are built from shapes rather than from bars with forged ends, in order that the floor beams may be attached to them with the same details that are used at other panel points. The following specifications apply:

§ 30. *Floor beam hangers, and other similar members (in tension), liable to sudden loading (plates and shapes) net section at 6,000 pounds per sq. in.*

Long verticals in tension (plates or shapes) net section at 9,000 pounds per sq. in. for live loads and 18,000 pounds per sq. in. for dead loads.

U_1L_1, L_4M_4 and L_6M_6 are long verticals and they are covered by the second of the preceding provisions.

Member U_1L_1.

Dead load stress	$= +33{,}000$ pounds.
Live load stress	$= +84{,}000$ pounds.
(1/2 dead + live) load stress	$= 100{,}500$ pounds.

$\frac{100{,}500}{9000} = 11.17$ sq. ins. required.

The following 15 inch channels spaced 14 inches back to back more than satisfy this requirement:

2, 15″ — ['s, weighing 32.95 pounds per lin. ft. @ 9.69 sq. ins. = 19.38 sq. ins. gross or 17.88 sq. ins., net, held together by single latticing 2¼ × ⅜ in.

This is much more metal than is needed, but the member is 36 feet long and requires increased stiffness on that account. As these same channels must be used for a number of the main web-members of the truss, they will also be used for these long verticals.

Members L_4M_4 and L_6M_6.

Both of these members are subjected to the same stresses, and since they occupy similar positions in the truss, they will be designed exactly alike.

Dead load stress = + 33,000 pounds.
Live load stress = + 84,000 pounds.
(1/2 dead + live) load stress = 100,500 pounds.
$\frac{100500}{9000} = 11.16$ sq. ins. required.

A narrower channel than 12 inches cannot be used on account of the floor beam connection; it will be necessary to use two 12-inch channels, each weighing 24.51 pounds per lin. ft., with a total gross area of 14.42 sq. ins. and a net area of 12.86 sq. ins. tied together by single latticing 2¼ × ⅜ in. These members will be continued vertically upwards to form the members M_4U_4 and M_6U_6 respectively; their sections are ample to carry the compressive stresses imposed.

ART. 9. DESIGN OF VERTICAL MAIN WEB MEMBERS OR POSTS.

U_2L_2, U_3L_3, U_5L_5.

These main vertical posts are all in compression and therefore subject to the following specification:

§ 33. All posts of through bridges shall be proportioned by the following allowed unit stresses:

$$P = 8{,}500 - 45\frac{l}{r} \text{ for live load stresses.}$$

$$P = 17{,}000 - 90\frac{l}{r} \text{ for dead load stresses.}$$

Member U_2L_2.

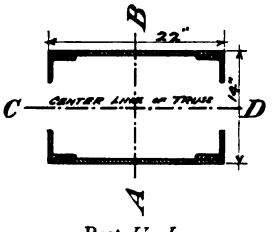
Dead load stress = — 98,000 pounds.
Live load stress = — 161,000 pounds.
(½ dead + live) load stress = — 210,000 pounds.

By assuming the width of post at 22 inches, and the radius of gyration .35 of this width, the length of the post being 540 inches, the allowed intensity of stress becomes

$P = 8{,}500 - \frac{45 \times 540}{7.7} = 5{,}340$ pounds per sq. in., and the area of section required $\frac{210{,}000}{5{,}340} = 39.3$ sq. in.

The following trial section (Fig. 3) may be assumed:

2 plates $22'' \times \frac{9}{16}''$ $= 24.75$ sq. ins.
4 angles $3\frac{1}{2}'' \times 3\frac{1}{2}'' \times \frac{9}{16}''$ $= 14.60$ sq. ins.
39.35 sq. ins.



Post U_2–L_2

FIG. 3.

The plates are spaced 14 inches back to back. The moment of inertia about the *AB* axis will be:

$$\text{Plates} = 2\left[\frac{\frac{9}{16} \times (22)^3}{12}\right] = 1{,}000.$$

$$\text{Angles} = 4\,[4.0 + (3.65 \times 10^2)] = 1{,}476$$

$$\text{Total} = 2{,}476.$$

$$\therefore r = \sqrt{\frac{2{,}476}{39.35}} = 7.95 \text{ ins.}$$

It will not be necessary to make use of the radius of gyration about the *CD* axis (in this case 6.48 inches) since the length of the column to be inserted in the formula, when considering this radius, is much reduced by the cross-bracing at its upper end. The allowed intensity of stress for this seortened column, taken in connection with the smaller radius of gyration, should always be tested.

In the present case, the value of 7.95 inches, for the *AB* radius, checks the value assumed sufficiently near so that recalculation will not be necessary; the trial section will be adopted as it stands using single $2\frac{1}{2} \times \frac{3}{8}$ in. lattice bars.

Member U_3L_3.

Dead load stress $= -32{,}000$ pounds.
Live load stress $= +25{,}000$ pounds.
Live load stress $= -73{,}000$ pounds.

In the case of this member, the following specification relative to alternate stress becomes operative:

§ 35. *Members subject to alternate stresses of tension and compression shall be proportioned to resist each kind of stress. Both of the stresses shall, however, be considered as increased by an amount equal to* $\frac{8}{10}$ *of the least of the two stresses for determining the sectional areas by the usual allowed unit stresses.*

The equivalent live load stress for U_3L_3 then becomes ($\frac{1}{2}$ dead $+ \frac{8}{10}$ tension live + compression live) load stress $= -109{,}000$ pounds.

Assuming a width of 15 inches, and the radius of gyration .35 the width, the length of the column being 27 feet (not 54 feet, since it is supported in two directions at the center) furnishes a unit stress of $8{,}500 - (45 \times 324)/5.25 = 5{,}720$ pounds per sq. in. The required area will therefore be

$$\frac{109{,}000}{5{,}720} = 19.0 \text{ sq. inches.}$$

A trial section of 2–15 in. channels, weighing 32.95 pounds per lin. foot, with a total area of section of 19.38 square inches will be found to furnish a radius of gyration of 5.67 inches, and to fulfill all the required conditions. The spacing back to back of channels will be made uniform with that of the other hangers and posts at 14 inches, and the latticing will be single, $2\frac{1}{2} \times \frac{3}{8}$ inches

Member U_5L_5.

Dead load stress $= -7{,}000$ pounds.
Live load stress $= +27{,}000$ pounds.
Live load stress $= -79{,}000$ pounds.

The equivalent live load stress is, $(\frac{1}{2} \times 7{,}000 + \frac{8}{10} \times 27{,}000 + 79{,}000) = 104{,}100$ pounds compression.

The effective length of column may be assumed as one half of 63 feet, and since the stress in U_5L_5 is nearly the same as that in U_3L_3, the section belonging to the latter may be used for a trial; therefore $r = 5.67$ inches. The allowed intensity of stress then becomes: $p = 8{,}500 - (45 \times 378)/5.67 = 5{,}500$ pounds per sq. in., and the area of cross-section required $104{,}100/5{,}500 = 18.95$ sq. ins.

The trial section of 19.38 sq. ins. may therefore be adopted as final, using as in the other cases a spacing of 14 inches back to back of channels, and single latticing 2½ inches by × ⅜ inch.

Tension Web Members, U_2L_3, U_3M_4, M_4L_5, U_5M_6.

The following specification applies to these tension web members:

§ *30. The allowed unit stresses in tension for main diagonals and counters shall be:*

10,000 pounds per square inch for live loads.

20,000 pounds per square inch for dead loads.

Member U_2L_3

Dead load stress = + 78,000 pounds.
Live load stress = + 160,000 pounds.

The equivalent live load stress is (½ dead + live) load stress = + 199,000 pounds.

The required order of cross-section will therefore be

$$\frac{199{,}000}{10{,}000} = 19.9 \text{ sq. ins.}$$

and will be formed of 2 eye-bars, 7 inches × $1\frac{7}{16}$ inches = 20.12 sq. ins.

The following table shows the method of design for the other web members.

Member.	Dead Load Stress in Pounds	Live Load Stress in Pounds.	Equivalent Live Load Stress in Pounds.	Area Required Square Inches.	Section Adopted.	Area of Final Section Square Inches.
U_3M_4	+90,000	+204,000	+249,000	24.9	2 bars — 7″ × $1\frac{13}{16}$″	25.38
M_4L_5	+57,000	+168,000	+196,500	19.65	2 bars — 7″ × $1\frac{7}{16}$″	20.12
U_5M_6	+36,000	+173,000	+191,000	19.1	2 bars — 7″ × $1\frac{3}{8}$″	19.26

ART. 10. DESIGN OF COUNTER MEMBERS, L_1U_3, L_3M_4, M_4U_5 AND L_5M_6.

The following specification applies to these members:

§ *45. The areas of counters shall be determined by taking the difference in areas due to the live and dead load stresses considered separately; the counters in any one panel must have a combined sectional area of at least three square inches, or else must be capable of carrying all the counter live load in that panel.*

Member L_2U_3.

There is actually no counter stress in the panel L_2L_3, and the member L_2U_3 is only inserted to secure a margin of safety. In compliance with the specifications, therefore, it must have a cross-section of at least 3 square inches. One adjustable rod 1¾ in. square, having an area of 3.06 square inches fulfills these requirements.

Member L_3M_4.

Dead load stress = — 90,000 pounds.
Live load stress = + 82,000 pounds.

The difference between the equivalent of the dead load stress in terms of the live load, and the live load will be — ½(90,000) + 82,000 = 37,000 pounds tension.

At 10,000 pounds per square inch, a cross-sectional area of 3.7 square inches will be required. Two adjustable rods 1½ inches square, having an area of cross-section of 4.5 square inches will be used.

The stress in the remaining counter members are not completely determined statically, and the sectional areas of those members should be based on the undiminished live load stresses in them.

Member L_5M_6.

Dead load stress = — 36,000 pounds.
Live load stress = + 136,000 pounds.

This member should be designed according to the last condition of the specification; viz., to be capable of carrying all the counter live load in the panel; the area required will therefore be 13.5 square inches, and will be composed of 2 adjustable bars 6 × 1⅛ ins., having an area of 13.5 square inches.

Member M_4U_5.

Live load stress = + 39,000 pounds,
Dead load stress = + 62,000 pounds,

or

Dead load stress = + 104,000 pounds,
Live load stress = — 66,000 pounds.

This member will be designed according to the same condition as L_5M_6. In this case all the counter live load stress equals 104,000 pounds, and at 10,000 pounds per square inch, the area required would be 10.4 square inches, which is supplied by two 6 × 1 in eye-bars having an area of 12 square inches.

This completes the design of the main members of the truss;

the intermediate struts M_3M_4, M_5M_6 and the collision strut supporting the center of the end post carry no definite stresses. Their form of section depends to a great extent upon their end connections, and they are usually built of light angles latticed together in box shape.

In the present case all these struts will be built of four $3\frac{1}{2} \times 3\frac{1}{2} \times \frac{5}{8}$ in. angles, having a combined area of 10 square inches laced together in a box form by four sets of single lacings $2\frac{1}{4} \times \frac{5}{16}$ in. The dimensions of the box forms will depend upon the connections which these struts make with other members.

ART. 11. COMBINED STRESSES.

§ 39. *When any member is subjected to the action of both axial and bending stresses, as in the case of end posts of through bridges, or of chords carrying distributed floor loads, it must be proportioned so that the greatest fiber strength will not exceed the allowable limits of tension or compression on that member. If the fiber stress resulting from weight only, of any member exceeds 10 per cent. of the allowed unit stress on such member, such excess must be considered in proportioning the areas.*

In accordance with the above specification, the chord members should be tested with reference to the bending stresses induced by their own weight. The condition of the ends or of the supported sections of these sections considered as beams is largely a matter of conjecture; they may be considered fixed at their ends, or assumed entirely free to turn, or their condition may be assumed half way between. It is probably reasonable, at least, to assume these members fixed at their ends or supported sections, since the friction on the pins will tend to produce that condition.

It will be sufficient for present purposes to test one upper and one lower chord member for combined stresses. The method here adopted for finding the bending stress in the truss members, although always yielding safe results, is not exact. Strictly speaking, the bending effect of the axial stresses should be recognized.*

Member U_5U_6.

The cross-sectional area of this number is 99.09 square inches but allowing 20 per cent. additional for rivets, latticing and other

* For exact theory, see Burr's "Resist. of Mat.," edition 1903, pp. 181.

details, the weight per inch of length will be 33.8 pounds. The length between centers of end pins is 350 inches; therefore the maximum bending moment M, assuming the member to have fixed ends, will be at the center, and equal to 518,000 inch pounds.

The moment of inertia I of the section is 12,254; therefore k, the intensity of stress in the extreme fibers is, by the following formula:

$$k = \frac{Md}{I} = \frac{518{,}000 \times 14}{12{,}254} = 592 \text{ pounds per square inch.}$$

This is less than 10 per cent. of the allowed compressive intensity in the member, and it may therefore be neglected.

Member L_5L_6.

The dimensions of one eye-bar are 8 in. deep × 1⅞ in. thick × 350 in. long; the weight per inch of length will be 4¼ pounds, and the maximum bending moment at the center, assuming fixed ends, will be 32,500 inch pounds. The amount of inertia is 80; therefore the stress in the extreme fibers at the center will be

$$\frac{32{,}500 \times 4}{80} = 1{,}625 \text{ pounds per squre inch.}$$

The permissible axial unit stress (see page 263) was 15,750 pounds per square inch, and the bending stress is so slightly in excess of 10 per cent. that it may be safely neglected.

There still remains to be treated the bending in the end post caused by the overturning effect of the wind; the maximum bending will occur at the connection of the curved bracket of the portal to the end post and at the foot of the end post, since that member may be considered fixed at the lower end, and also fixed in direction from the extreme upper end to the bracket connection. A point of contraflexure midway between the foot of the end post and the curved bracket may therefore be assumed to exist.

If it be supposed that the wind loads of the upper chord are carried equally to both end posts, the maximum bending moment becomes ½ wind reaction by ½ the distance along the post measured from its foot to the bracket connection; in this case 14,875 pounds × 140 inches = 2,082,500 inch pounds. The moment of inertia about the axis of bending is about 12,500, and the distance from the neutral axis to the extreme fiber of the upper angles is 15 inches, it being remembered that the bending takes place in the

plane at right angles to the vertical plane through the axis of the truss. The stress in the extreme fiber will then be

$$\frac{2{,}082{,}500 \times 15}{12{,}500} = 2{,}500 \text{ pounds per square inch.}$$

At the same time the stress in the web plates, which constitute the greater portion of the cross-section of the post, will be $(2{,}082{,}500 \times 11.5)/12{,}500 = 1{,}920$ pounds per square inch, due to this same bending.

This stress is a wind stress, and is therefore subject to § 36 of the specifications. The average stress in the end post due to dead and live loads is $(371{,}000 + 528{,}000)/97.25 = 9{,}250$ pounds, and one quarter of this is 2,310 pounds; therefore the bending due to wind may be safely neglected. As a further margin of safety it should be noted that the point of greatest bending due to wind does not coincide with the point of greatest bending due to the simple compression in the member.

ART. 12. DESIGN OF STRINGERS AND FLOOR BEAMS.

The following specifications apply to these members:

§ 30. The allowed unit stress in tension, for the bottom flanges or riveted cross girders (net section), shall be 10,000 pounds per square inch, and for the bottom flanges of riveted longitudinal plate girders used as track stringers (net section), 10,000 pounds per square inch.

§ 40. In beams and plate girders the compression flanges shall be made of the same gross section as the tension flanges.

§ 41. Riveted longitudinal girders shall have, preferably, a depth not less than of one tenth the span.

§ 42. Plate girders shall be proportioned upon the supposition that the bending or chord stresses are resisted entirely by the upper and lower flanges, and that the shearing or web stresses are resisted entirely by the web plate; no part of the web plate shall be estimated as flange area.

The distance between centers of gravity of the flange area will be considered as the effective depth of all girders.

§ 43. The webs of plate girders must be stiffened at intervals of about the depth of the girders, wherever the shearing stress per square inch exceeds the stress allowed by the following formula:

Allowed shearing stress =

$$\frac{12{,}000}{1 + \frac{H^2}{3{,}000}}$$

where H = *ratio of depth of web to its thickness; but no web plates shall be less than* ⅜ *of an inch in thickness.*

The following specifications for riveting also apply to the design of these members:

§ *37. The rivets in all members, other than those of the floor and lateral systems, must be so spaced that the shearing stress per square inch shall not exceed 9,000 pounds; nor the pressure on the bearing surface (diameter* × *thickness of the piece) of the rivet hole exceed 15,000 pounds per square inch.*

The rivets in all members of the floor system, including all hanger connections, must be so spaced that the shearing stresses and bearing pressures shall not exceed 80 per cent. of the above limits.

In the case of field riveting (and for bolts) the above-allowed shearing stresses and pressures shall be reduced one third.

Rivets and bolts must not be used in direct tension.

The stringers are assumed 350 inches long and 32¼ inches back to back of angles, the depth of the stringer being taken a little less than one tenth of the span to permit the required track elevation. The actual depth of the web plate will be 32 inches, but the distance back to back of angles is increased by ¼ inch, so that the web will not project between the angles, and cause difficulty in riveting the cover plates. It should be noted that shallow stringers deflect more than deeper ones, thus tending to produce greater direct tensile stresses on the end connection rivets.

The maximum bending moment due to live load will be found for that position of loading in which the center of gravity of the load is situated as far on one side of the center of the beam as the point of maximum bending is on the other side, and a wheel load will always be found over this point of maximum bending. In the present case, this point is found 14.2 ft. from the left end of the stringer under the second driver of the locomotive, as shown by Fig. 4.

The reaction at the left end of the stringer for this position of the loading is 43,800 pounds; the maximum bending moment is then found as follows:

$$M = 43{,}800 \times 14.2 - 10{,}000 \times 13 - 20{,}000 \times 5 = 392{,}000 \text{ ft. lbs.}$$
$$= 4{,}704{,}000 \text{ in. lbs.}$$

The dead load bending moment at the same point may be taken equal to the maximum dead load bending moment at the center, and is found as follows:

The track is assumed to weigh 400 pounds per lin. ft. and both stringers, and bracing 375 pounds per lin. ft. The weight per lin. inch per stringer will then be 32.29 pounds and the maximum moment:

$$\frac{32.29 \times (350)^2}{8} = 494{,}000 \text{ in. lbs.}$$

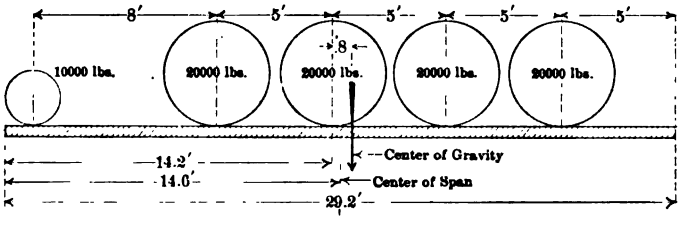


FIG. 4.

The effective depth of the girder according to the specifications may be assumed at 30 inches, and since the allowed intensity of stress is 10,000 pounds per sq. in., the required net section will be:

$$\frac{4{,}704{,}000 + 494{,}000}{30 \times 10{,}000} = 17.3 \text{ sq. ins.}$$

This flange or chord area will be afforded by 2 angles $6 \times 6 \times \frac{9}{16}''$ having a gross section of 13 sq. ins. = 10.7 sq. ins. net, and 1 cover plate $14 \times \frac{9}{16}''$ having a gross section of 7.9 sq. ins.= 6.8 sq. ins. net. Total, 17.5 sq. ins. net.

Length of Cover Plate.

The length of the cover plate will be determined by assuming that the bending moment follows a parabolic law. If L represents the total length of the stringer, l the length of the cover plate, A the total section of the flange, and a the total area of all the cover

plates counting from the outside and including the area of the one under consideration, then

$$l = L\sqrt{\frac{a}{A}}.$$

Inserting the requisite quantities in the formula,

$$l = 29.2\sqrt{\frac{6.8}{17.3}} = 18.3 \text{ feet.}$$

At least six inches should be added to each end of the completed length of a cover-plate in which to place additional rivets, so that the plate may actually develop its full strength at the section where it is needed. The length of the cover-plate in this case will therefore be 19.3 feet.

Web Plate.

The maximum shear for both dead and live loads occurs at the end of the stringer. The live load shear with the first driver at this point is 62,500 pounds. The dead load shear is 5,700 pounds, thus making the total shear 68,200 pounds. The working shear in the web plate may be taken at 5,000 pounds per square inch of gross section. The required cross-section will then be 13.6 square inches, and the web plate will be taken $32 \times \frac{7}{16}''$ = 14.0 sq. ins. According to the specifications, if the shearing stress exceeds $12{,}000/[1 + (H^2/3{,}000)]$, intermediate stiffeners will be required. In the present case this formula has a value of $12{,}000/1 + [(73.2^2/3{,}000)] = 4{,}310$ pounds per square inch, whereas the actual intensity of shear in the stringer is 5,000 lbs. per square inch at the ends, with a constantly decreasing value towards the center of the stringer; no intermediate stiffeners will therefore be required. The end stiffeners cannot be subjected to a rational analysis; in the present case they will be composed of two $6'' \times 6'' \times \frac{7}{16}''$ angles, being chosen of such dimensions as to permit of making simple connections to the floor beams. They are sometimes designed by requiring that their normal section must carry the end reaction with a certain specified unit process (as 7,000 pounds per square inch). In this case the normal section is 10.12 inches, and it is ample for the purpose.

Riveting.

The following rule will determine the pitch in the flanges of a girder; viz., the pitch of the riveting at any section of the flanges

will be the quotient obtained by dividing the product of the vertical distance between the rows of riveting in the two flanges and the allowed stress in one rivet either for shear or bearing, by the maximum shear at the section. This rule is readily demonstrated by taking the difference between the bending moments at two adjacent rivets.

In the present case the pitch at the ends of the stringer will be

$$\frac{30 \times (5{,}740 \times 80\%)}{68{,}200} = 2''.1.$$

At 10 feet from the ends the dead load shear will be 1,925

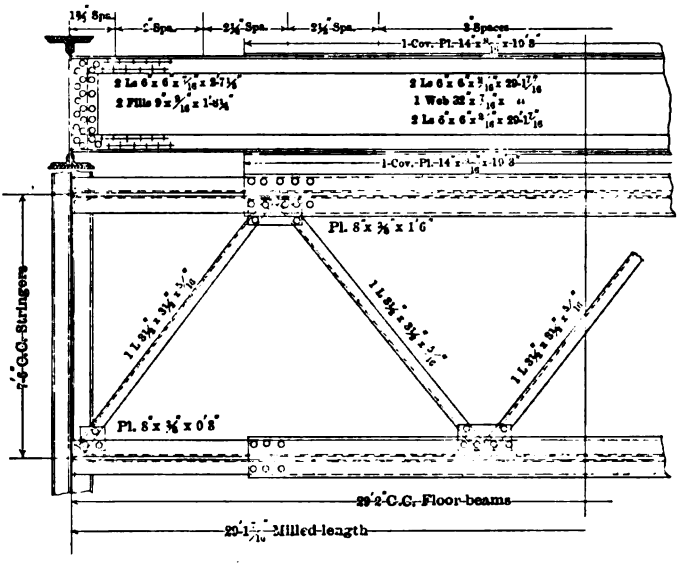


FIG. 5.

pounds, and the maximum live load shear, with the first driver over the section, will be 31,300 pounds.

The pitch at this point will therefore be

$$\frac{30 \times (5{,}740 \times 80\%)}{31{,}300 + 1{,}925} = 4''.15.$$

The flange rivets have thus far been considered to carry the direct horizontal stress only, but those in the upper flange must also carry as a vertical load the weight of the driving wheels as they pass. One driver, weighing 20,000 pounds, may be supposed to be distributed over three ties, or over a distance of 3 feet, as-

suming 6-inch spaces between ties 8 inches wide. The greatest effect in increasing the pitch will be found at the center of the girder. At this point 9 rivets would approximately be required in a distance of 3 feet, if the longitudinal stress alone existed; and 20,000/4,592 = 4.4 rivets for the vertical load alone. The proper number of rivets for this distance of 3 feet is then $\sqrt{9^2 + 4.4^2} = 10$. It is seen that the effect of this vertical loading in increasing the number of rivets is very small. The spacing finally adopted is shown in Fig. 5; it varies from $1\frac{3}{4}$ inches at the ends to 3 inches at the center, and more than provides for vertical load effect.

Rivets in Cover Plates.

The stress carried by the cover plate will be 6.8 square inches × 10,000 pounds = 68,000 pounds. The permissible stress in the rivets will be determined for single shear, at 80 per cent. of 5,410 pounds = 4,328 pounds per rivet. Sixteen rivets will be required. They will be placed in four rows with 3 inches pitch for a distance of 15 inches from the ends of the plate, and 6 inches pitch for the remaining distance.

Rivets on End Connection.

The rivets fastening the stringers to the floor beam are field rivets, and therefore the allowed intensities of stress in them must be reduced one third.

Two separate conditions effect the number of rivets at this end connection; first, the single shear on these rivets when one stringer has its maximum reaction, and secondly, the bearing on the web of the floor beam, when the combined reactions at the two stringer ends resting on the floor beam have their maximum value. For the first case, each rivet in a single shear will carry 5,410 × .8 × $\frac{2}{3}$ = 2,885, and with a maximum end reaction of 68,200 pounds, there will be required 24 rivets; in the second case, assuming the thickness of the floor beam web plate at $\frac{9}{16}$ inch, the bearing capacity of one rivet will be 7,380 × .8 × $\frac{2}{3}$ = 3,930 pounds; the simultaneous maximum combined reactions of the two stringers will be, for dead load 14,000 pounds, and for live load 84,000 pounds (see design of floor beam for these reactions), or a total of 98,000 pounds; there will therefore be required 25 rivets. Thirteen rivets will however actually be placed in each 6 × 6 inch angle, making 26 rivets at this connection.

The bill of material with the weights for one stringer, and ½ the cross bracing, using that indicated in Fig. 5 for which no actual design will be made, may be written as follows:

		Lbs. per Ft.		
1 web plate $32 \times \frac{7}{16}''$	29.1	ft. long @	50.58 =	1,470 lbs.
4 angles $6 \times 6 \times \frac{9}{16}''$	"	" " @	21.9 =	2,550 "
2 cover plates $14 \times \frac{9}{16}''$	19.25	" " @	26.78 =	1,060 "
4 end stiffeners $6 \times 6 \times \frac{7}{16}''$	2.6	" " @	17.2 =	178 "
4 filling plates $6 \times \frac{9}{16}''$	1.6	" " @	11.48 =	74 "
2½ bracing angles $3\frac{1}{2} \times 3\frac{1}{2} \times \frac{5}{16}''$	—9.5	" " @	2.1 =	50 "
About 450 pairs of ⅞″ rivet heads	@ 22.2 lbs. per 100 =			200 "
				5,582 lbs.

The actual weight per foot of stringer is thus seen to be 384 pounds, or 9 pounds per foot more than was assumed. This difference is so small as to require no correction in the design, but it is better to have the actual weight under rather than over the assumed.

Intermediate Floor Beams.

The maximum live load floor beam reaction occurs when wheel 5 is placed directly over the floor beam. Wheels 1 to 4 will then be on one adjoining stringer and wheels 5 to 9 on the other, making the resulting reaction 84,000 pounds.

Assuming the dead weight of the floor beam to be 300 pounds per lin. ft., the dead load reaction will become:

Dead weight of one stringer = 11,300 pounds.
Dead weight of ½ floor beam = 2,700 "
14,000 pounds.

The sum of the dead and live load reactions will then be 98,000 pounds.

The stringers are spaced 7 feet 6 inches apart, and since the distance between trusses is 18 feet, the stringer is distant 63 inches from the center line of the truss. Therefore the maximum bending of the floor beam will be 98,000 × 63 = 6,170,000 in. lbs. Assuming an effective depth of 42 inches, the flange area required will be 6,170,000/42 × 10,000 = 14.69 sq. ins. This section will be composed of 2 angles 6″ × 4″ × ½″ = 9.6 sq. ins. gross = 8.6 sq. ins. net; 1 cover plate 14″ × ½″ = 7.0 sq. ins. gross = 6.0 sq. ins. net Total, 14.6 sq. ins. net.

The cover plate should have the following length:

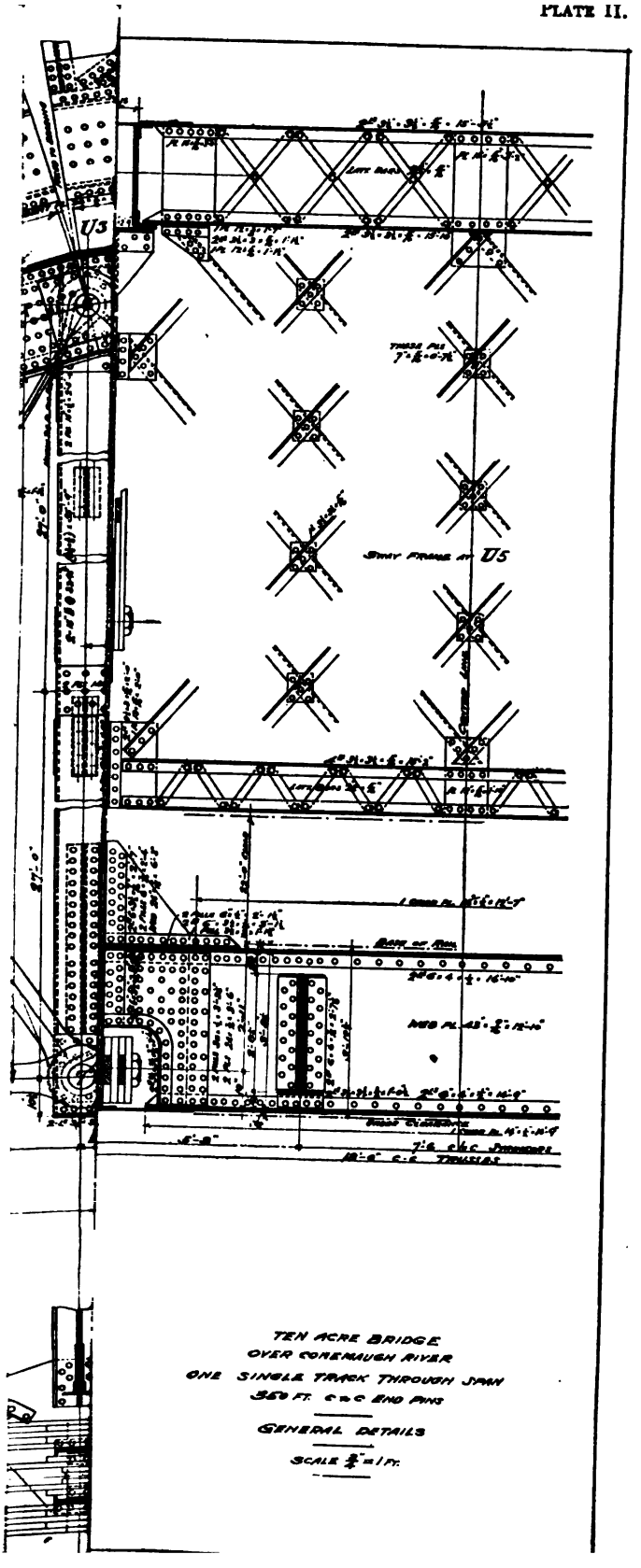
$$l = 18 \sqrt{\frac{6}{14.6}} = 11.5 \text{ feet};$$

owing to the details at the ends of the floor beam the upper cover plate will have a length of 12 feet 7 inches and the lower a length of 14 feet 9 inches.

On account of the large number of rivets made necessary at the end connection of the floor beam, and the consequent weakening of the plate, the assumed intensity of shearing stress for the web has been taken at 4,000 pounds per square inch of gross section. The area required will therefore be 98,000/4,000 = 24.5 square inches, and a plate 43 by $\frac{9}{16}$ inch = 24.2 square inches will fulfill the requirements. No intermediate stiffeners will be required, as the end connections of the stringers render end stiffeners unnecessary. The distance from back to back of the flange angles will be 43½ inches. At the connection of the floor beam to the post, a considerable portion of the web plate must be removed in order to leave room for the heads of the lower chord eye-bars. It is therefore customary to cut the web plate at some distance from the end, and to splice to it another plate of irregular shape having an equal cross-sectional area. The general detail drawing, Plate II., illustrates the method adopted in the present case. The central portion of the web is 10 feet 12 inches long and spliced to it at each end by means of two $\frac{7}{16}$-inch plates, placed over ½-inch fillers, is another plate designated on the figure as "web 24 inches × $\frac{9}{16}$ inches × 6 feet 3 inches long." To this end web plate are fastened the end stiffeners formed of two 6 × 3½ × $\frac{7}{16}$ inch angles. The end stiffener must be divided into an upper and lower part in order to allow the upper flange of the floor beam to abut against the post. The lower portion of the end web plate will be cut away with rounded edges, to the form required by the disposition of the eye bars, all floor beams being made alike to conform to that post in which the greatest clearance is required. This edge will be protected by two angles 3½ inches × 3½ inches × ⅜ inch, and 3 feet 6 inches long. The lower flange of the floor beam will be connected to the foot of the post by a flat plate riveted to both, to provide against swaying, and to form part of the lower lateral wind system.

Riveting.

Instead of employing the rule used in finding the pitch of the rivets in the flanges of the stringers it will be better to divide the amount of stress in the flanges of these beams between the post connection and the stringer connection, by the allowed stress


U3
U5
TEN ACRE BRIDGE
OVER CONEMAUGH RIVER
ONE SINGLE TRACK THROUGH SPAN
359 FT. c. to c. END PINS
GENERAL DETAILS
SCALE 1/4" = 1 FT.

capacity of one rivet; the quotient will determine the number of rivets between these two points. For example:

$$\frac{146{,}900}{7{,}380 \times .8} = 25 \text{ rivets.}$$

These are easily provided for in the lower flange, but a pair of supplementary angles $6 \times 3\frac{1}{2} \times \frac{7}{16}$ inch and 3 feet 1½ inches long must be fastened to the upper flange at its ends in order to provide for the requisite rivets to transfer the stress from the web plate to the flanges. The rivet design of this end connection is not very precise. The rivets piercing the spliced central portion of the web plate of the floor beam really aid in carrying the stress through the splice plate to the flanges. It is essential that all parts at this point shall be firmly and rigidly tied together. The pitch in the central portion of the beam will be 6 inches.

The number of rivets necessary on each side of the splice will be

$$\frac{98{,}000}{7{,}380 \times .8} = 17,$$

and they will be placed in two rows, as shown in Plate II.

At least the same number of rivets will be necessary to fasten the end stiffeners to the web plate; but since 17 rivets cannot be placed in one row, the two rows shown on the plate will be inserted, even though all those there shown are not necessary. The resulting surplus may be considered as compensating for the tendency to pull on the rivet-heads, due to the deflection of the loaded beam.

The end stiffeners are connected to the post by field rivets. The thickness of the web of the post is three eighth inch, but this thickness will be increased by a diaphragm which will later be inserted between the channel webs, so that the single shear of the rivets determines their number.

The rivets required will therefore be $[98{,}000/(5{,}410 \times .8 \times \frac{3}{8})] = 34$.

The rivets in the cover plate will be pitched 3 inches for a distance of 15 inches from the ends of the cover plate, and 6 inches for the remaining distance.

A small angle bracket consisting of a $3\frac{1}{2} \times 3\frac{1}{2} \times \frac{3}{8}''$ angle 1 foot 0½ inches long will be riveted to the floor beam to form a seat for the ends of the stringer during erection. This bracket is

used for temporary convenience only, and is not supposed to carry any stress after erection.

It is sometimes customary, if web plates have no splices, to take one sixth [or sometimes one eighth] of the web section as acting in either flange. If no rivet holes were punched for the stiffeners, this method would be allowable. But such rivet holes frequently take out considerable metal, and as the tension side of the plate only is affected, one sixth of the remaining metal ceases to be a proper proportion. On the whole, therefore, it is better to neglect the bending resistance of the web, and allow it to balance, so far as it may, the effect of the rivet holes being out of the center of gravity of the flange angles.

The bill of material and the weight of the floor beam is given in the following table:

	Length.	Weight per Foot	Total Weight.
1 Web plate 43″ x $\frac{9}{16}$″	12′ 10″	82.24	1040
2 " plates 24″ x $\frac{9}{16}$″	6′ 3″	45.90	573
2 Flange angles 6″ x 4″ x ½″	16′ 10″	16.2	545
2 " " "	14′ 9″	16.2	478
1 Cover plate 14″ x ½″	12′ 7″	23.8	300
1 " " "	14′ 9″	23.8	350
4 End stiffening angles 6″ x 3½″ x $\frac{7}{16}$″	1′ 8¾″	13.5	90
4 " " " "	2′ 7″	13.5	140
4 " fillers 6″ x $\frac{7}{16}$″	2′ 4″	8.93	83
4 " finishing angles 3½″ x 3½″ x ⅜″	3′ 6″	8.5	119
4 Splice plates 24″ x $\frac{7}{16}$″	3′ 6″	35.70	500
4 Filling plates 30″ x ½″	3′ 3″¼	51.00	660
4 Upper flange, end angles 6″x3½″x$\frac{7}{16}$″	3′ 1½″	13.5	163
4 " " fillers 6″ x ½″	2′ 1½″	10.20	86
2 " " " 3½″ x $\frac{9}{16}$″	1′ 1½″	6.70	15
4 Bracket angles 3½″ x 3½″ x ⅜″	1′ 0½″	8.5	35
340 prs. of rivet heads at 22.2 lbs. per 100			150
			5,327 lbs.

The assumed weight is 5,400 pounds *i. e.*, greater than the actual, as it should be.

AN ELEMENTARY LECTURE ON THE METHOD OF LEAST SQUARES.*

By HAROLD JACOBY.

Introductory. — Probably the best way to approach this subject is to begin by considering a concrete example derived from actual experience. For this purpose, let us use a time determination made with the ordinary portable transit instrument and chronograph. Employing the usual notation, we put:

ΔT = the chronometer correction,

α, δ the star's right ascension and declination,

a, b, c = the azimuth, level and collimation corrections of the transit,

φ = the latitude,

T = the observed time of transit of any star.

Now, introducing the three "star-constants":

$$A = \frac{\sin(\varphi - \delta)}{\cos \delta}, \quad B = \frac{\cos(\varphi - \delta)}{\cos \delta}, \quad C = \frac{1}{\cos \delta},$$

we have, omitting corrections for rate and diurnal aberration:

$$T + \Delta T + Aa + Bb + Cc - \alpha = 0.$$

If we now let the letter t represent the sum of all known quantities, or:

$$t = T + bB - \alpha,$$

the above equation becomes:

$$\Delta T + Aa + Cc + t = 0, \qquad (1)$$

and an equation of this form will result from each star observed.

The quantities appearing in this equation are of three kinds with respect to our knowledge as to their numerical values.

1. Unknown quantities; viz.: ΔT, a and c.

2. A quantity known from observation, and therefore subject to errors of observation; viz.: t.

3. Coefficients known with practically complete accuracy from theory; viz.: A and C.

* This lecture is intended primarily for students of geodesy. Those unacquainted with astronomical notation may omit to equation (1).

Let us now re-write equation (1) repeating it several times with subscript numbers, so as to separate equations depending on the successive stars observed. We have:

$$\begin{aligned} \Delta T + A_1 a + C_1 c + t_1 &= 0, \\ \Delta T + A_2 a + C_2 c + t_2 &= 0, \\ \Delta T + A_3 a + C_3 c + t_3 &= 0, \\ \Delta T + A_4 a + C_4 c + t_4 &= 0, \\ \text{etc.} \qquad \text{etc.} & \end{aligned} \tag{2}$$

It is at once evident that as we have only three unknown quantities (ΔT, a, and c) we can compute their numerical values from any three equations of the group (2) by the ordinary processes of elimination given in elementary algebras. But which three equations shall we select for this purpose? We might use the first three, for instance, or the last three, or the first equation and the last two. If we try the actual process numerically upon a real example we generally find that the values of the unknowns come out different from the various combinations of equations. It was not until the Method of Least Squares was introduced that astronomers had a better way of reducing their observations than the crude one of solving a great many different combinations, and then taking the mean of the results so obtained.

The reason for the differences thus arising from different combinations of equations is easy to find. We have seen that the quantities t in equations (1) and (2) are known from observation, and therefore subject to the usual small unavoidable observational errors. If the t's were absolutely correct, all combinations of equations would give precisely the same results for the three unknowns. But the t's are not thus absolutely correct; and, in a very strict sense, the several equations numbered (2) are therefore inconsistent amongst themselves. Admitting fallible numerical values of the t's as actually observed, all equations of the form (2) cannot be exactly true simultaneously: indeed, it follows from the very nature of observational errors such as affect the t's, that in all probability no one of the equations (2) is really absolutely correct and true.

The right-hand members of equations (2), then, should not really be zeros. It will be more correct to represent them by a series of small quantities v, and to write equations (2) thus:

$$\begin{aligned} \Delta T + A_1 a + C_1 c + t_1 &= v_1, \\ \Delta T + A_2 a + C_2 c + t_2 &= v_2, \\ \Delta T + A_3 a + C_3 c + t_3 &= v_3, \\ \Delta T + A_4 a + C_4 c + t_4 &= v_4, \\ \text{etc.} \qquad & \text{etc.} \end{aligned} \tag{3}$$

Formation of Normal Equations. — It will be convenient at this point to introduce a change of notation, so as to give greater generality, and at the same time avoid the somewhat cumbersome notation so far used. It will be remembered that this latter has been employed simply to visualize our conceptions by fixing attention upon an example derived from our own actual practice. We shall now designate the unknown quantities we desire to determine by the letters x, y, z, instead of $\Delta T, a$, and c: and the known coefficients of x, y, z, we shall designate by the letters a, b, c, instead of 1, A, and C. The quantities t, observationally known, will now be designated by n's. This will bring us into uniformity with the usual practice of writers on Least Squares. Our general equations intended for solution thus become, from (3):

$$\begin{aligned} a_1 x + b_1 y + c_1 z + n_1 &= v_1, \\ a_2 x + b_2 y + c_2 z + n_2 &= v_2, \\ a_3 x + b_3 y + c_3 z + n_3 &= v_3, \\ a_4 x + b_4 y + c_4 z + n_4 &= v_4, \\ \text{etc.} \qquad & \text{etc.} \end{aligned} \tag{4}$$

The v's are here simply the errors of the equations, if we may be permitted the use of such an expression. More accurately, they are the amounts by which the equations fail of satisfaction when we substitute in them any assumed system of numerical values for the unknowns x, y, z. If, by any process whatever, we obtain a system of numerical values for x, y, z, and substitute those values in the left-hand members of equations (4), we shall obtain a series of residual errors represented by the v's. The name "residual" has therefore been given to the v's, for brevity.

It is evident that if we consider two different systems of numerical values for the unknowns x, y, z, and substitute both systems in equations (4), we shall get two different sets of values for the re-

siduals v. In fact, and in general, for every different system of values belonging to x, y, z, there will be a different set of v's: it is the province of the Method of Least Squares to determine which system of x, y, z, and corresponding v's is preferable. To do this, we make use of the following principle, due to Legendre:

Of all possible systems of values for the unknowns x, y, z, that one possesses the highest probability of being correct which makes the sum of the squares of the residuals v a minimum.

This principle does not admit of rigorous demonstration, but it is so highly plausible that we are justified in adopting it without hesitation. This plausibility becomes evident when we consider that the best system of values for x, y, z, must certainly make all the individual residuals small. Yet it would not do to adopt as our principle that the sum or mean of the residuals should be a minimum. For some being positive, and some negative, it might happen that the sum or mean would be made very small, while the individual v's remained in part very large. But the squares are not subject to this criticism, since they are all positive, and are at the same time the simplest functions that are thus positive.

Adopting, then, Legendre's principle of Least Squares, it remains to show how we can use it to solve equations (4). We shall employ square brackets as a symbol of summation, so that, for instance, the quantity

$$[vv]$$

will designate the sum of the squares of all the v's. Then, according to Legendre's principle, we must have:

$$[vv] = \text{a minimum.} \tag{5}$$

But, according to equations (4), $[vv]$ is a function of x, y, z, and as these latter quantities are independent variables, the principles of maxima and minima in the calculus tell us that we can satisfy the condition (5) by equating separately to zero the first partial differential coefficients of $[vv]$ with respect to x, y, z. In other words, we have:

$$\frac{\partial [vv]}{\partial x} = 0, \qquad \frac{\partial [vv]}{\partial y} = 0, \qquad \frac{\partial [vv]}{\partial z} = 0. \tag{6}$$

Now since:

$$[vv] = v_1 v_1 + v_2 v_2 + v_3 v_3 + v_4 v_4 + \text{etc.}$$

equations (6) become:

$$\begin{aligned} v_1\frac{\partial v_1}{\partial x} + v_2\frac{\partial v_2}{\partial x} + v_3\frac{\partial v_3}{\partial x} + \text{etc.} &= 0, \\ v_1\frac{\partial v_1}{\partial y} + v_2\frac{\partial v_2}{\partial z} + v_3\frac{\partial v_3}{\partial y} + \text{etc.} &= 0, \\ v_1\frac{\partial v_1}{\partial z} + v_2\frac{\partial v_2}{\partial z} + v_3\frac{\partial v_3}{\partial z} + \text{etc.} &= 0. \end{aligned} \tag{7}$$

Now, differentiating equations (4), we have:

$$\begin{aligned} \frac{\partial v_1}{\partial x} &= a_1, & \frac{\partial v_1}{\partial y} &= b_1, & \frac{\partial v_1}{\partial z} &= c_1, \\ \frac{\partial v_2}{\partial x} &= a_2, & \frac{\partial v_2}{\partial y} &= b_2, & \frac{\partial v_2}{\partial z} &= c_2, \\ \frac{\partial v_3}{\partial x} &= a_3, & \frac{\partial v_3}{\partial y} &= b_3 & \frac{\partial v_3}{\partial z} &= c_3; \\ \text{etc.} & & \text{etc.} & & \text{etc.} & \end{aligned}$$

so that (7) become:

$$\begin{aligned} a_1v_1 + a_2v_2 + a_3v_3 + \text{etc.} &= 0, \\ b_1v_1 + b_2v_2 + b_3v_3 + \text{etc.} &= 0, \\ c_1v_1 + c_2v_2 + c_3v_3 + \text{etc.} &= 0. \end{aligned} \tag{8}$$

It will be noticed that the number of equations of the form (8) is the same as the number of unknown quantities x, y, z, no matter how large may have been the number of original equations of the form (4). We shall therefore simply substitute in equations (8) values of the v's from equations (4), remembering that, according to our notation:

$$\begin{aligned} [aa] &= a_1a_1 + a_2a_2 + a_3a_3 + \text{etc.}, \\ [ab] &= a_1b_1 + a_2b_2 + a_3b_3 + \text{etc.}, \\ [ac] &= a_1c_1 + a_2c_2 + a_3c_3 + \text{etc.}, \\ & \text{etc.} \qquad\qquad \text{etc.} \end{aligned}$$

and thus obtain the following equations:

$$\begin{aligned} [aa]x + [ab]y + [ac]z + [an] &= 0, \\ [ab]x + [bb]y + [bc]z + [bn] &= 0, \\ [ac]x + [bc]y + [cc]z + [cn] &= 0. \end{aligned} \tag{9}$$

Equations (9) are called "Normal Equations." As we have just seen, their number is always equal to the number of unknown quantities, and their solution by elimination offers no ambiguity. Furthermore, owing to the method by which they have been deduced, it is clear that they will furnish for the unknowns x, y, z, a system of numerical values, which, when substituted in the original equations (4), will make the sum of the squares of the residual errors less than would be the case with any other possible system of numerical values for the unknowns, no matter how such other system might have been obtained.

If we now compare the above normal equations (9) with the original equations (4), which are usually called "observation equations," we see at once the law of formation of (9) from (4). It is evident that to form the normal equations we may use the following simple rule, first writing zeros instead of v's for the right-hand members of equations (4).

Rule for normal equations. — To form the first normal equation multiply each observation equation throughout by the coefficient of its x, and then add the resulting equations. To form the next normal, use in the same way the coefficients of y; and for the third normal use the coefficients of z.

The normal equations once formed, they can be solved by any method of algebraic elimination; but it is generally most convenient to use the following special form of computation, due to Gauss.

From the first equation (9) we have:

$$x = -\frac{[ab]}{[aa]}y - \frac{[ac]}{[aa]}z - \frac{[an]}{[aa]}.$$

If we substitute this value of x in the other two normal equations (9) we shall eliminate x. This substitution can be systematized by the introduction of auxiliary quantities $[bb\cdot 1]$, $[bc\cdot 1]$, etc., defined by the following equations:

$$[bb\cdot 1] = [bb] - \frac{[ab]}{[aa]}[ab], \quad [bn\cdot 1] = [bn] - \frac{[ab]}{[aa]}[an],$$

$$[bc\cdot 1] = [bc] - \frac{[ab]}{[aa]}[ac], \quad [cn\cdot 1] = [cn] - \frac{[ac]}{[aa]}[an]. \quad (10)$$

$$[cc\cdot 1] = [cc] - \frac{[ac]}{[aa]}[ac],$$

Using these auxiliaries, the substitution of the above value of x gives:

$$\begin{aligned} [bb \cdot 1]\, y + [bc \cdot 1]\, z + [bn \cdot 1] &= 0. \\ [bc \cdot 1]\, y + [cc \cdot 1]\, z + [cn \cdot 1] &= 0. \end{aligned} \tag{11}$$

These equations, while precisely similar in form to the original normal equations (9), now involve one less unknown quantity, and their number has been reduced from three to two. A second application of the same method of elimination gives the following "second" auxiliaries:

$$\begin{aligned} [cc \cdot 2] &= [cc \cdot 1] - \frac{[bc \cdot 1]}{[bb \cdot 1]} [bc \cdot 1], \\ [cn \cdot 2] &= [cn \cdot 1] - \frac{[bc \cdot 1]}{[bb \cdot 1]} [bn \cdot 1], \end{aligned} \tag{12}$$

and the equation:

$$[cc \cdot 2]\, z + [cn \cdot 2] = 0. \tag{13}$$

From this equation (13), we have for the value of z:

$$z = -\frac{[cn \cdot 2]}{[cc \cdot 2]}. \tag{14}$$

We now find the value of y by substituting this value of z in either of the equations (11); and x by substituting the values of y and z in any one of the normal equations (9).

Case of a Single Unknown.—It is of especial interest to consider the application of the Method of Least Squares when there is only a single unknown quantity, directly observed. An example of this, for instance, would be the measurement of a base line, where the only unknown is the length of the base, and several independent direct observations of this length have been made.

Denoting the single unknown quantity by x, the observation equations of the form (4) will be:

$$\begin{aligned} x + n_1 &= v_1, \\ x + n_2 &= v_2, \\ x + n_3 &= v_3, \\ x + n_4 &= v_4, \\ &\text{etc. etc.;} \end{aligned} \tag{15}$$

and if we suppose there are in all m such observation equations, the "rule for normal equations" gives a single normal equation of the form:

$$mx + [n] = 0, \tag{16}$$

and this will be the only normal equation. It gives the solution:

$$x = -\frac{[n]}{m}, \tag{17}$$

or, in other words, the most probable value of x is the arithmetical mean of the several observed values represented by the n's. This is a further strong addition to the evidence of plausibility attaching to Legendre's theorem of Least Squares. Probably no other simple admissible theorem as to the residuals would give this result for a single unknown, observed directly; yet this result is the only one consistent with common sense.

Actual, Mean, and "Probable" Errors. — The values obtained for the unknowns by the Method of Least Squares are not the true values, but only the "most probable" values obtainable under the circumstances. They are subject to error; and we shall here consider three different quantities technically known as "Errors."

1. The *actual error*, defined as the divergence from the truth, and designated by the symbol Δ.

2. The *mean error*, defined as an error of such magnitude that its square is the mean of the squares of all the actual errors Δ belonging to the several observations. It is designated by the symbol ε. If there are m Δ's,

$$\varepsilon\varepsilon = \frac{[\Delta\Delta]}{m}. \tag{18}$$

3. The *probable error*, whose magnitude is such that it is an even chance whether any random actual error Δ is bigger or smaller than the probable error. It is designated by r.

To determine the value of ε we proceed as follows. Let:

x_0 = the arithmetical mean of the observed values of the unknown x, equation (17).

$x_0 + q$ = the unknown and unknowable true value of x.

Then, as we have seen, x_0 is the most probable value of x, according to the Method of Least Squares, and $[vv]$ will be a minimum if we substitute that value of x in equations (15). This substitution gives:

$$x_0 + n_1 = v_1,$$
$$x_0 + n_2 = v_2,$$
$$x_0 + n_3 = v_3,$$
$$\text{etc.}$$

But if, instead of x_0, we substituted the true quantity $x_0 + q$, we should get a series of true errors Δ, instead of the residuals v. This would give:

$$x_0 + q + n_1 = \Delta_1,$$
$$x_0 + q + n_2 = \Delta_2,$$
$$x_0 + q + n_3 = \Delta_3,$$
$$\text{etc.}$$

A subtraction between these last two sets of equations gives:

$$\Delta_1 = v_1 + q,$$
$$\Delta_2 = v_2 + q, \qquad (19)$$
$$\Delta_3 = v_3 + q,$$
$$\text{etc.}$$

and there will be m such equations. Squaring and adding them gives:

$$[\Delta\Delta] = [vv] + mq^2 + 2[v]q$$

But, from the principle of the arithmetical mean,

$$[v] = 0,$$

so that:

$$[\Delta\Delta] = [vv] + mq^2. \qquad (20)$$

From the equation of definition (18):

$$[\Delta\Delta] = m\varepsilon\varepsilon;$$

so that,

$$\varepsilon\varepsilon = \frac{[vv]}{m} + q^2 \qquad (21)$$

Now, the value of q can never be known; but we can get an approximation to it easily enough. It can be shown by the theory of probabilities that if we continue observing any quantity, the mean error of the arithmetical mean of the observed values will decrease in proportion to the square root of the number of observations.

To demonstrate this principle, let us consider:

Two observed quantities,	n_1, n_2,
affected with actual errors,	Δ_1, Δ_2,
and mean errors,	ε_1, ε_2.

Now let N be the sum of n_1, and n_2, or:

$$N = n_1 + n_2,$$

and designate by Δ' and ε' the actual and mean errors of N. We shall have:

$$\Delta' = \Delta_1 + \Delta_2;$$

and squaring this equation:

$$\Delta'\Delta' = \Delta_1\Delta_1 + \Delta_2\Delta_2 + 2\Delta_1\Delta_2.$$

If k observations have been made to determine n_1 and n_2, the above becomes by summation:

$$[\Delta'\Delta'] = [\Delta_1\Delta_1] + [\Delta_2\Delta_2] + 2[\Delta_1\Delta_2].$$

In this equation, the last term, $2[\Delta_1\Delta_2]$, may be considered zero, because it will disappear, or nearly disappear, in the general average, on account of positive and negative errors being equally probable, *a priori*. But the squared terms remain, being always positive, and we have:

$$[\Delta'\Delta'] = [\Delta_1\Delta_1] + [\Delta_2\Delta_2].$$

Consequently, by our equation of definition (18), this becomes:

$$\varepsilon'\varepsilon' = \varepsilon_1\varepsilon_1 + \varepsilon_2\varepsilon_2.$$

This equation brings out the important principle that the square of the mean error of the sum of two quantities is equal to the sum of the squares of their respective mean errors. The principle can of course be extended so as to include three, or any greater number, say m, of observed quantities.

Now let us suppose the n's to have been observed with equal accuracy, so that ε_1 and ε_2 will be equal, and we have:

$$\varepsilon'\varepsilon' = 2\varepsilon_1\varepsilon_1,$$

or for m n's:

$$\varepsilon'\varepsilon' = m\varepsilon_1\varepsilon_1,$$

or

$$\varepsilon' = \sqrt{m}\,\varepsilon_1$$

This last equation shows that the mean error ε' of the sum of m equally precise quantities is $\sqrt{m}$ times the mean error of one quantity. But the arithmetical mean of m observations is $1/m$ times their sum, and its mean error therefore ε'/m, or, according to the above:

$$\text{Mean error of arithmetical mean} = \frac{\varepsilon_1}{\sqrt{m}}.$$

which establishes the principle enunciated above, that the mean error of the arithmetical mean decreases in proportion as the square root of the number of observations increases.

In accordance with this principle, x_0 will be more accurate than any individual average x in the proportion of $\sqrt{m}$ to 1. Consequently, since q is the error of x_0, and ε a sort of average value for the error of any x, we may take as a good approximation for q:

$$q = \frac{\varepsilon}{\sqrt{m}}.$$

Substituting this value of q in equation (21), we get:

$$(m - 1)\varepsilon\varepsilon = [vv],$$

or:

$$\varepsilon = \sqrt{\frac{[vv]}{m - 1}}; \qquad (22)$$

and equation (22) will enable us to calculate approximately the mean error ε from the known residuals v.

It would carry us too far afield in the theory of probabilities to demonstrate the relations existing between the mean error ε and the probable error r. But we may remark in passing that it is shown in works on the theory of errors, that, approximately:

$$r = \tfrac{2}{3}\varepsilon,$$

or

$$r = \tfrac{2}{3}\sqrt{\frac{[vv]}{m - 1}}, \qquad (23)$$

Furthermore remembering that ε and r have reference to the precision attainable from a single observation, we can get the corresponding errors belonging to the arithmetical mean from m observations by the aid of the principle already used, viz.: that the diminution of error is proportional to the square root of the number of observations. Denoting the mean and probable errors of the arithmetical mean from m observations by ε_0 and r_0, equations (22) and (23) give:

$$\varepsilon_0 = \sqrt{\frac{[vv]}{m(m - 1)}}, \qquad (24)$$

$$r_0 = \tfrac{2}{3}\sqrt{\frac{[vv]}{m(m - 1)}}, \qquad (25)$$

Mean and Probable Error for Several Unknowns. — Equation (22), so far as we have yet considered it, applies only to the case of a single unknown x observed directly m times. But a similar expression can also be found for the case of observation equations of the form (4), when solved by means of normal equations of the form (9). Having found values of the unknowns x, y, z, from the solution of normal equations, we substitute these values in the original observation equations, and thus obtain numerical values of the residuals v, by which amounts the original observation equations fail of being exactly satisfied. With these values of the v's we form $[vv]$. If we then let

μ = the number of unknown x, y, etc., appearing in the original observation equations,

it may be shown that we shall have for the mean and probable errors:

$$\varepsilon = \sqrt{\frac{[vv]}{m - \mu}}, \tag{26}$$

$$r = \tfrac{2}{3}\sqrt{\frac{[vv]}{m - \mu}}. \tag{27}$$

For the complete demonstration of these equations we must refer to works on the Method of Least Squares. The equations furnish average approximate values for the mean and probable errors of any average observed quantity n, as it appears in any observation equation of the form (4). The unknowns x, y, z, are of course determined from the whole group of equations with much greater precision, and therefore with smaller mean and probable errors. In the case of z, for instance, it is shown in works on Least Squares that its mean and probable errors are smaller than those given by (26) and (27) in the proportion of:

$$[cc.2] \text{ to } 1,$$

where $[cc.2]$ is the final coefficient of z appearing in the last reduced equation (13) resulting from the Gaussian elimination of the normal equations (9). Consequently, denoting by ε_z and r_z the mean and probable errors of z, we have:

$$\varepsilon_z = \sqrt{\frac{[vv]}{[cc.2](m - \mu)}}. \tag{28}$$

$$r_z = \tfrac{2}{3}\sqrt{\frac{[vv]}{[cc.2](m - \mu)}}. \tag{29}$$

The corresponding mean and probable errors of x and y can be found by re-arranging the observation equations in such a way that each unknown in turn will come out last in the Gaussian elimination.

Weights. — It happens sometimes that the quantities n, appearing in the observation equations (4), have been determined by the observers with unequal precision. For instance, a certain n may have been observed twice, while all the others depend upon a single observation only. In such a case, that particular n is said to have "double weight," or the weight 2, while all others have the weight 1 only. Obviously, we can treat this case in our reductions by simply writing the doubly weighted equation *twice*, with all its coefficients and unknowns, among the observation equations, and then proceeding as usual. There is, however, a better way of dealing with this matter of varying weights; and we can derive it from a careful consideration of the rule for the formation of normal equations from observation equations. We may use the following:

Rule for Weighting Observation Equations. — Multiply each observation equation throughout by the square root of its weight, and then form normal equations by the usual rule.

It may be seen readily, in the simple case of one equation only having double weight, that this rule will produce precisely the same effect on the normal equations as would result from merely writing that particular observation equation twice among the other observation equations, in the manner just explained. But it is also shown in works on Least Squares that the above rule for weights holds good when all the observation equations have different weights, and even when these weights are fractional.

Numerical Example. — To illustrate the foregoing, Mr. A. D. Butterfield, graduate student of astronomy, made a set of observations with the Bamberg universal transit of the Columbia University observatory, on February 25, 1904. After the application of preliminary corrections for level, he obtains the following equations of the form (2), the letters W and E indicating the position of the instrument during the observation of each star.

$$\nu \text{ Aurigæ} \quad (\text{W}), \quad \Delta T + 0.04a + 1.29c - 0^{s}.27 = 0,$$

$$\theta \text{ Aurigæ} \quad (\text{W}), \quad \Delta T + 0.08a + 1.26c - 0.02 = 0,$$

$$22 \text{ H. Camel.} \quad (\text{W}), \quad \Delta T - 1.36a + 2.84c - 6.52 = 0,$$

$$\begin{aligned}
\psi' \text{ Aurigæ} \quad (W), \quad & \Delta T - 0.23a + 1.54c - 1.32 = 0, \\
51 \text{ Aurigæ} \quad (W), \quad & \Delta T + 0.03a + 1.30c + 0.06 = 0, \\
\psi^5 \text{ Aurigæ} \quad (E), \quad & \Delta T - 0.07a - 1.30c - 0.02 = 0, \\
\theta \text{ Geminor.} \quad (E), \quad & \Delta T + 0.14a - 1.21c + 0.84 = 0, \\
63 \text{ Aurigæ} \quad (E), \quad & \Delta T + 0.03a - 1.30c + 0.48 = 0, \\
64 \text{ Aurigæ} \quad (E), \quad & \Delta T - 0.01a - 1.33c + 0.31 = 0, \\
1308 \text{ Groombr.} \quad (E), \quad & \Delta T - 1.28a - 2.75c - 4.68 = 0.
\end{aligned} \tag{2'}$$

Applying to these the "Rule for Normal Equations," gives:

$$\begin{aligned}
+ 10.00\,\Delta T - 2.63a + 0.34c - 11^s.22 &= 0, \\
- 2.63\,\Delta T + 3.59a - 0.63c + 15.30 &= 0, \\
+ 0.34\,\Delta T - 0.63a + 29.43c - 9.78 &= 0.
\end{aligned} \tag{9'}$$

The method of equations (10) and (11) transforms these into the following:

$$\begin{aligned}
+ 2.90a - .54c + 12^s.35 &= 0 \\
- .54a + 29.42c - 9.40 &= 0.
\end{aligned} \tag{11'}$$

A further application of (12) gives:

$$+ 29.32c - 7.10 = 0. \tag{13'}$$

From this we obtain:

$$c = + 0^s.24. \tag{14'}$$

If we now substitute this value of c in either of equations (11') we obtain:

$$a = - 4^s.25.$$

These values of a and c can now be substituted in either of equations (9'), and we get:

$$\Delta T = - 0.^s005.$$

We now substitute the numerical values thus obtained for c, a, and ΔT in equations (2'), and obtain the following residuals, v:

	v'	vv'
ν Aurigæ	$0^s.125$	0.015625
θ Aurigæ	.055	.003025
22 H. Camel.	.075	.005625
ψ' Aurigæ	.025	.006250
51 Aurigæ	.125	.015625

ψ^5 Aurigæ	.005	.000025
θ Geminor.	.045	.002025
63 Aurigæ	.045	.002025
64 Aurigæ	.025	.000625
1308 Groombr.	.125	.015625
	Sum	.060850

Applying equation (27), remembering that m is the number of residuals, in this case 10, we have:

$$r = \tfrac{2}{3}\sqrt{\frac{.060850}{10-3}} = \pm 0^s.061 \qquad (27')$$

This is the "probable error" of a single observation. To obtain the corresponding quantity for the value of c, given by equation (14') we must use equation (29). We have from (13'):

$$[cc.2] = 29.32.$$

Consequently, from (29):

$$r_c = \tfrac{2}{3}\sqrt{\frac{.060850}{29.32(10-3)}} = \pm 0^s.011 \qquad (29')$$

This result signifies that it is an even chance whether the actual error of our numerical value of c is greater or less than $0^s.011$, so that the probable error becomes a sort of test of the precision of our result.

To obtain the probable error of another unknown, as ΔT, we rearrange the equations (2') so as to make ΔT the last unknown, instead of c. Written in this way, the equations are:

$$\begin{array}{c} +\ 0.04a + 1.29c + \Delta T - 0^s.27 = 0, \\ \text{etc.} \qquad\quad \text{etc.} \end{array} \qquad (2'')$$

The normal equations are:

$$\begin{array}{rrrr} 3.59a - & .63c - & 2.63\Delta T + & 15.30 = 0 \\ -\ .63a + & 29.43c + & .34\Delta T - & 9.78 = 0 \\ -\ 2.63a + & .34c + & 10.00\Delta T - & 11.22 = 0 \end{array} \qquad (9'')$$

The method of equations (10) and (11) gives:

$$\begin{array}{rrr} 29.32c - & .12\Delta T - & 7.10 = 0 \\ -\ .12c + & 8.07\Delta T - & .01 = 0 \end{array} \qquad (11'')$$

The application of (12):

$$8.07\,\Delta T - .01 = 0. \qquad (13'')$$

And, consequently:

$$\Delta T = +\,0^{s}.00, \qquad (14'')$$

This is practically the same as the value already obtained, and thus affords incidentally a very complete check on arithmetical accuracy. Values of c and a can of course be obtained as before by substitution.

Applying equations (29) again we have the probable error of ΔT.

$$r_{\Delta T} = \tfrac{2}{3}\sqrt{\frac{.060850}{8.07(10-3)}} = \pm\,0^{s}.022 \qquad (29'')$$

Equation (14″) shows that the clock was exactly right; and (29″) that the precision of this clock-error determination is very high.

ALUMINOTHERMICS.*

By DR. HANS GOLDSCHMIDT.

The two elements of most frequent occurrence on our planet are oxygen and aluminum. By producing in a suitable manner the chemical combination of these two, a temperature is created, which is about equal to that of the electric arc. On this discovery is based the new science called aluminothermics. Which is the proper manner of combining aluminum with oxygen? By taking not the atmospheric oxygen but the solid oxygen contained in the oxides; these are mixed with finely granulated or pulverized aluminum. The resulting mixture is the heat producer and is called thermit. (Reg. Trade Mark.)

The next aim is to produce this great heat in the simplest and most efficacious manner and then to discover the fields in which it can be applied to most advantage.

The first important discovery in observing the properties of this mixture — thermit — was that, when ignited in one spot, the com-

* Illustrated lecture given by the inventor, Dr. Hans Goldschmidt, of Essen, Germany, in Havemeyer Hall, Friday evening, November 13, before the Columbia University Chemical Society.

bustion continued throughout the whole mass without any supply of heat from outside. The mass is placed in crucibles which are not in contact with any external source of heat, and the combustion, once started, embraces the whole mass in a very short time. This is the essence of aluminothermics.

FIG. 1. Sternpost of S. S. Sevilla Welded in Dry Dock.

Experiment I. Igniting thermit. — In the crucible there are then two layers. The bottom one is pure metal (in this case iron) of equal weight to, but occupying only one third as much space as the top layer which is now oxide of aluminum, so-called corundum.

To demonstrate the heat created by this chemical reaction I will now burn a hole through a one-inch wrought-iron plate.

Experiment II. — You will notice that the crucible is tapped from the bottom so as to allow the pure iron, which has a temperature of about 3,000° C. (5,400° F.), to run out at first. The hole is perfectly smooth-edged; the heat is so concentrated that the plate is still cold after the reaction.

Fifty years ago attempts were made to apply the reducing properties of aluminum. Without exception the experimenters heated their compounds externally. The reaction was always so violent that they could only operate with very small quantities. It will therefore easily be seen that to arrive at aluminothermics from such a starting point required patient study and assiduous work. Each of the mixtures, although made according to simple chemical rules, required studying out by itself. Boys will try to make gunpowder according to old Berthold Schwartz's receipt by mixing saltpeter, charcoal and sulphur. They will succeed in producing some powder of sufficient explosive force to burn their fingers, but I think the United States Navy would have no use for it.

In all such exothermic processes the physical properties of the ingredients in this case, particularly those of the oxides, want considering. Then the methods of manufacture have to be worked out for each case.

In the following I am going to illustrate by practical demonstration a few of the applications of the thermit process; to give an account of the entire field of its utility would go beyond the scope of a single lecture. The applications may be roughly divided into two main divisions, the one concerning the metallurgist, the other the engineer. The latter application may be summarized in the word "welding." The study of the metallurgical application preceded that of the other by a few years.

Amongst the pure metals produced by the alumino-genetic reaction I may mention in the first instance chromium free from carbon, as having already found a market in this country. It is used in the manufacture of particular qualities of chromium steel with a limited percentage of carbon. For instance, it is considerably used for self-hardening tool steel with five to six per cent. chromium, about twice that quantity of tungsten and only 0.6–0.7 carbon.

Pure manganese also produced by this process finds employment in copper and nickel manufacture and, furthermore, in the production of particular sorts of manganese steel of great strength and great elasticity with twelve to fourteen per cent. manganese.

Pure molybdenum and ferro-vanadium have also lately been put on the market. Ferro-titanium has been in use with a number of steel works for quite a considerable time. The peculiar application of titanium by means of its thermit will be dealt with later on.

A number of metals or alloys are also produced, among which I will mention ferro-boron, manganese-boron, lead-barium, although their value for practical purposes is limited at present. The experiments with boron are not yet concluded.

I shall now show you one of these reactions; the one with nickel thermit. Its slag is distinguished by a beautiful blue color on account of its containing traces of cobalt.

Experiment III. — Although this demonstration is only on a very small scale, it will prove that the process is an extremely simple and expeditious one. In actual manufacturing several hundred-weight are produced in one reaction. At the end of the lec-

FIG. 2. Rail Welding on Track with Clamps.

ture the mass will have cooled sufficiently for me to show the regulus of pure nickel. The slag covering this regulus, particularly in making chromium, is utilized as an artificial emery on account

of its great hardness. It has been given the name of corubin. It has also refractory properties which have been utilized in various manners.

The first division appertaining to metallurgy I shall now abandon for the present in order to acquaint you with the process which has received the widest attention and practical application. I mean the thermit welding process.

Considering the innumerable details connected with the application of so new and practically unknown a force, it is not surprising that only since about a year ago the process has been introduced on a large and commercial scale.

The most important of these welding processes is the one by which a continuous rail — a necessity of modern trolley road construction — is simply, cheaply and effectively obtained. Engineers in this country, in which no less than 25,000 miles of single track are in existence, are watching the good results obtained in Europe with this system. European authorities recognize its advantages over all its competitors.

The city of Leeds, in England, after careful investigation by a committee of experts, is using this process over the whole of its track, and an American expert who had occasion to see it employed there, on his own initiative, recommended it for a very important contract at Singapore, where, in consequence, it is being used over a track of twenty-seven miles. Last year 3,000 joints were welded, and this year no less than 20,000 joints have been delivered.

FIG. 3. Side of Rail Showing Weld.

What gives this system an advantage over all others is the absence of any bulky equipment; all that is required is a crucible, a mould-box, and in some instances, where a complete butt-weld of

the head of the rail is desired, a rail-clamp. All these materials, including the necessary quantity of thermit, can easily be moved on a hand truck. Each weld, according to section, requires from fifteen to twenty pounds of thermit.

Even where a rail clamp is used the time employed is less than that necessary for fixing fishplates and copper bonds.

The mould is made according to a model designed specially for each section. Its two parts, one on each side, firmly enclose and exactly fit the rail. Certain channels are provided in the mould-

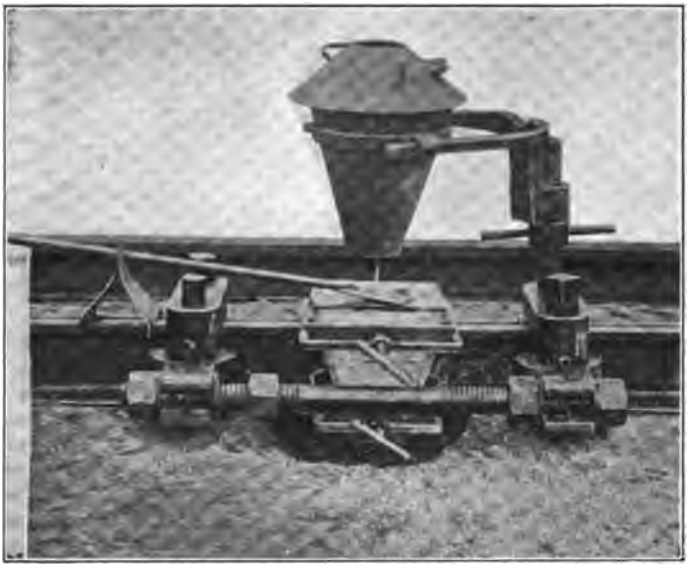


FIG. 4. Complete Outfit for Rail Welding.

parts for the thermit iron to run through. The size of these chan nels, which are open towards the rail, has been accurately determined by experiments. It varies according to whether slag or iron is to fill the mould and also in accordance with the requirements of each section. The thermit iron running out of the crucible flows round the web and foot of the rail and, melting them, forms one mass with them. The liquid slag which follows the metal is diverted to the top of the rail and brings the latter to welding heat. The whole section is thus heated equally and the rail ends will not buckle.

The weld can be made with or without rail clamps. In the former case the rail ends are butted together by tightening the screw

two or three minutes after the run. A slight and very short upset will be produced at the joint, which can easily be removed. The simplest way has been found to chisel it off; a grinder does not answer the purpose equally well. One man can even out twenty-five joints in a day in this manner. By using the rail clamps a perfect butt weld, without even the smallest slit, is obtained. The rigidity of the joint is particularly great. Under hydraulic pressure the break occurs outside the welded zone, as with the iron shoe welded on to the section the joint is really stronger than the rail.

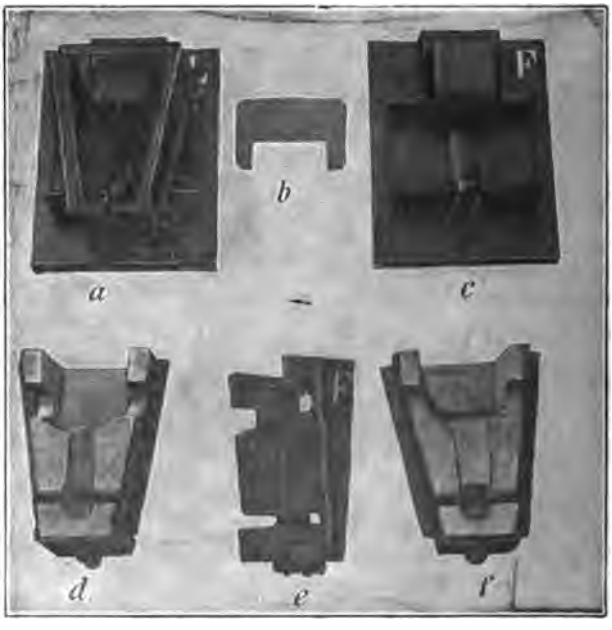


FIG. 5. Rail Welding Process. *a*, model for the lip side with mould shell; *b*, appliance used when ramming the sand in; *c*, model for tread side; *d*, finished half of mould for lip side; *e*, half of mould shell for tread side; *f*, finished half of mould for tread side.

The use of the rail clamps is, however, by no means obligatory. Without them the work is still further simplified, as the time necessary for adjusting the heavy clamps and for chiseling off the upset is saved. By practical experience it has been found that the weld without clamps is quite sufficient. Of late the clamps are being used less and less.

The first to weld without clamps was the town of Brunswick, Germany, more than two years ago; it has continued to follow

this plan ever since. Nearly all the work done in France, such as at Rouen, Havre and Paris, was without clamps, and the joints have now been in the ground for more than a year. Italy also, particularly the cities of Genoa and Milan, preferred to work without clamps. Altogether this mode has been tried in several thousand joints and given entire satisfaction.

The use of clamps is based chiefly on theoretical considerations. Even a butt-weld can be obtained without clamps, particularly with rails already embedded. At Barmen, Germany, such work was done very successfully about a year and a half ago. The old fish-plates were taken off, the ends of the rails were raised slightly by

FIG. 6. Rail Welding Without Clamps.

means of a crowbar, and a shim firmly wedged in between; in this case the shim is welded into the head of the rail.

When welding new rails not yet embedded the use of rail clamps can be obviated by firmly wedging up the rail from the next succeeding joint.

Working without clamps the time consumed per joint equals three quarters of an hour for one man; trained squads of four men, including foreman, did not use nearly so much time. At $1.50 per day the wage item is ten cents per joint. The use of the clamps doubles this amount. All other labor connected with welding remains the same whether clamps are used or not.

To come back to the moulds. They are made in two parts, as I told you a little while ago. They can either be made on a large scale by manufacturers of refractory earthenware, or according to momentary requirements by the trolley lines in their own shops. In the latter case they are made by ramming an ordinary mixture of sand and loam into a sheet-iron case, which afterward has to be dried during a couple of hours at a temperature of some 100° C. The cost of the mould is, therefore, only a few cents.

The mould, in a good, dry and porous condition, is screwed on to the rail and the rims touching the rail are carefully smeared with clay. Before doing so, however, the rail ends are cleaned of dirt and rust with a wire brush and slightly warmed; a sand blast is superfluous. In case the tops of the rails are to be butt-welded the section has to be filed.

This is all that is required in the way of preparatory work. A true alignment of the rail is, of course, an indispensable precaution. The rails require no bolt holes, as no provisional fish-plates are necessary.

FIG. 7. Conical Crucibles Lined with Magnesia.

You will recognize that none of this work demands special training, and that the trolley companies' men here, as in Europe, will be easily able to do it. A certain supervision to see that it is done carefully is a matter of course.

In case of wet weather the protection of a few planks is desirable to prevent the mould and thermit getting wet.

The next and only remaining appliance necessary for thermit welding is the crucible. This consists of a sheet iron mantle lined with magnesia. It is of simple construction, the lining being introduced by tamping it round a cone which is suspended in the

middle of the mantle. The bottom is formed by a hard magnesia stone provided with an exchangeable outlet, which will stand nine to ten runs. The crucible with the cone in it is placed in the furnace for only two hours and finally brought to glow heat. It is then ready for use. Trolley lines who have adopted the system on a large scale all make their own crucibles. Crucibles will stand about twenty-five reactions, and the wear and tear will, therefore, amount to only a few cents per joint. Every section, according to its weight and according to its different dimensions, requires different quantities of thermit, the composition of which has also to be regulated for each separate case. It is supplied in small bags containing the exact weight which is needed to effect the weld. These are called welding portions and are sold as such to the trolley companies. The companies who make their own crucibles and moulds will, therefore, have to pay freight only on the welding portions. As these weigh about twenty pounds gross, the freight is, of course, considerably less than that on fish-plates and bolts. Mr. Cole, the engineer in charge of the construction of the Singapore Tramways, who, as I mentioned, is welding all his joints by the Thermit Process, writes as follows under date of October 10, 1903: "We have not had one pull apart, a thing that would occur very quickly if the weld was not all that was required, for we have large sections exposed to the weather for days without being covered up, and the contractive force of the changes of temperature, would quickly pull the joints apart if they were not well done. The joints are nearly all done in the heat of the day, when the metal is expanded to its maximum limit. We have a difference of over 60 degrees between night and day." I shall now show you how a rail is welded.

Experiment IV. Rail welding. — The strength of the weld is about eighty per cent. of the strength of the original material. The shoe welded on to the foot of the rail not only makes up for the remaining twenty per cent. but materially strengthens the rail at the joint. The head does not get softer although it is brought to welding heat; the reason being that the operation takes place without the air having access to it. Test rods cut out of rails brought to welding heat with thermit prove this contention. Tensile strength and elasticity have not suffered.

Three years' practical experience on the road confirms these tests, over forty towns in Europe having utilized the system.

Strength of Thermit Joint.*

June 23, 1903.

Rail supported five feet center to center test made with ten-inch ram, two-inch bearing on head of rail.

Up to 28 tons, no deflection and no set, and then $\frac{1}{64}$ inch.
" " 30 " $\frac{1}{32}$ inch.
" " 40 " $\frac{1}{32}$ inch.
" " 45 " $\frac{1}{64}$ inch.
" " 50 " $\frac{3}{32}$ inch.
" " 55 " $\frac{3}{32}$ inch.
" " 60 " $\frac{1}{8}$ inch.

Test was then stopped, and it was found that there was no permanent set whatever.

Pressure brought on again to sixty-five tons, still only one eighth inch deflection.

At 68 tons rail still sound.
" 70 " " broke, not through the weld.

July 7, 1903.

Hydraulic test. Dead load. Five feet bearings, ten-inch ram, two-inch bar on head of rail.

85 tons .... $\frac{3}{16}$ inch set.
90 " .... $\frac{1}{4}$ inch "
95 " .... $\frac{1}{2}$ inch and slight fracture.

Thermit-welded joint tested to dead load as above.

Up to 60 tons no permanent deflection.
Safe dead load at 68 tons.
70 tons fractured at side of the weld, the welded portion remaining intact.

Fish and sole plate joint. Fish plates 62 lb. per pair, 2 feet long, six 1-inch bolts; sole plate 46 lb., 2 feet by 8 inch by 3/4 inch, 12 7/8-inch bolts.

Permanent set at 85 tons $\frac{3}{4}$ inch.
" " " 90 " $\frac{7}{8}$ inch.
Fractured at 102 tons.

---

*Tests made by Mr. F. S. McGregor, Permanent Way Engineer, Leeds City Tramways.

J. S. McGregor, Permanent Way Engineer.

The so-called third rail is also welded by this means. The skin resistance of copper bonds increases with time and frequent repairs are necessitated thereby. Welding obviates these repairs. It can be done in two ways. The first is identical with the one described before (but without the use of clamps) and is now in operation on twenty miles of road at Paris, France, where a short track gave satisfaction after a year's trial. The second consists in welding a small bridge of thermit iron between the feet on one side of the rail. Both are in use on a large scale. On the suburban road from Berlin to Grosslichterfelde, The Union Electr. Ges. of Berlin has welded thirteen and a half miles of track. In this case the crucible is superfluous. The welding portion of about three pounds only is placed directly into the upper part of the mould, which is prolonged by a piece of gas pipe.

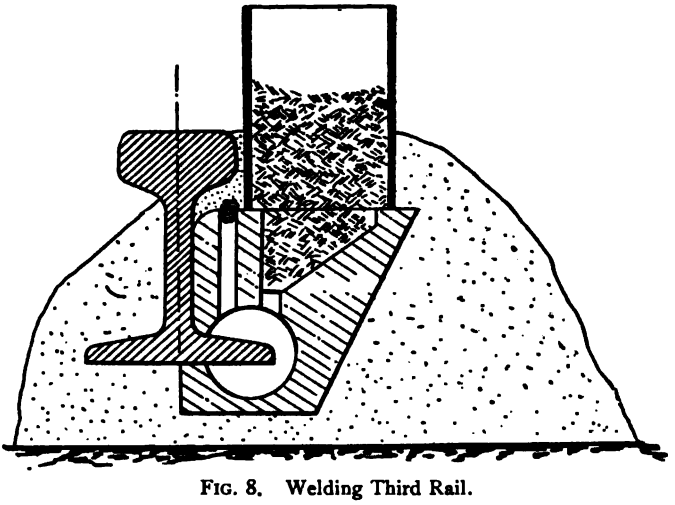


Fig. 8. Welding Third Rail.

Experiment V. Third rail. — You see it takes less time to perform the experiment than to describe it.

The next field of application I shall now touch upon is an exceedingly wide one. I mean the repair of solid iron and steel objects. Thermit, as I told you, gives fifty per cent. of mild, very overheated steel with 0.1 carbon, which can be hardened if desired, for instance by an addition of manganese. Whoever has a supply of thermit has a supply of liquid steel. Accordingly foundries can correct faulty castings, machine shops can mend broken or

worn-out parts, and last but not least marine engineering works can repair large steel castings, such as crank shafts, and particularly broken stern posts. In a test of thermit, made by the Pennsylvania Railroad Company in Altoona, the riser from the weld of the steel frame was drawn out under the hammer into a bar some three feet long and turned down and broken. The analysis of the metal is as follows:

Carbon	0.102 per cent.
Manganese	2.330 "
Phosphorus	0.070 "
Silicon	1.227 "
Sulphur	0.034 "

The following was the result of the physical test:
Tensile strength in pounds per square inch, 91,600.
Elongation in 8 inches, 21.5 per cent.
Appearance of fracture, silky.

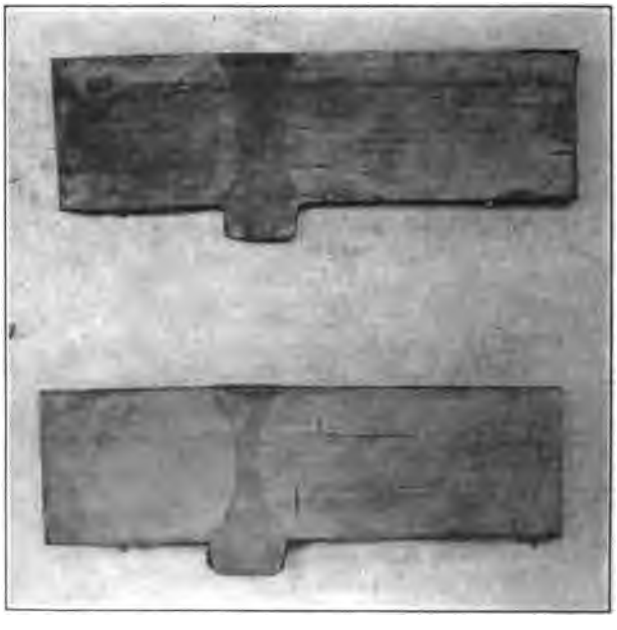


FIG. 9. Intermediate Weld of Rectangular Rods, 5½ in. by 5⅛ in.

Wherever the distance from construction shops is a matter of consideration and in all outlying districts this thermit is of particular value. Within the last few months regular ton orders have been received from South Africa, where damaged machinery of all

FIG. 10. Repair of a Large Engine Wheel.

kinds has been repaired by it in the mining districts. In many cases cast iron has been welded.

Certain rules have to be observed in all repair work. First and foremost the slag should not be allowed to get mixed up in the plastic iron. An appropriate position of the runner and a little experience in the construction of the most effective shape of mould will prevent this. These sketches will show some of the various shapes of moulds.

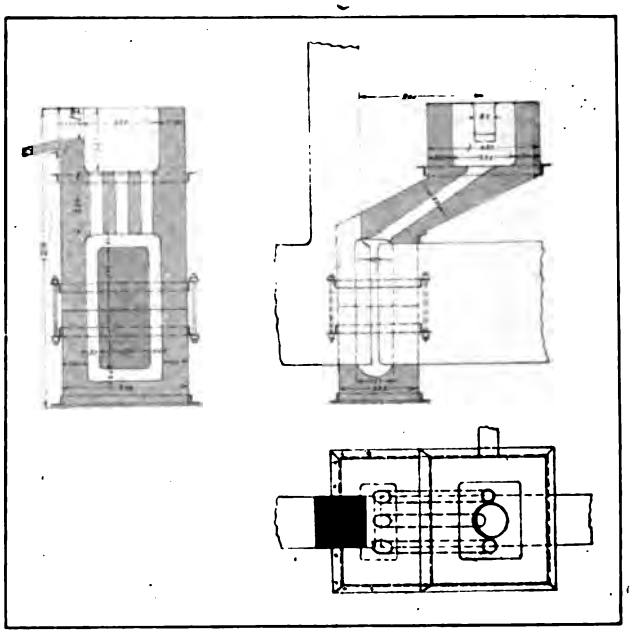


FIG. 11. Mould for Sevilla Repair.

The most startling and at the same time most effective work done in the way of repairs by thermit is in connection with marine engineering. To weld broken stern-posts of the big transatlantic liners or crank-shafts or similar pieces, crucibles containing seven cwt. of thermit and 6 feet high have had to be made. The reaction in these takes hardly longer than the one you saw here just now. The enormous advantage offered to steamship owners by such repairs will be apparent when it is remembered that a broken stern-post would otherwise have to be replaced by a new one. Besides this expense, the one incurred through loss of time, the steamer being

laid up in dry dock for weeks and weeks in order to have the new part fitted in, is very heavy indeed.

Experiment VI. Welding Thermit Iron on Steel Plate. — An application where Thermit may be ignited on the object is in repairs of broken roll bosses. The roll is firmly fixed so that the welding surface lies horizontally. The mould carries on its inside, suspended by an overlapping rim, an iron ring of one-half inch diameter. After this mould and ring are firmly fixed, a one-half

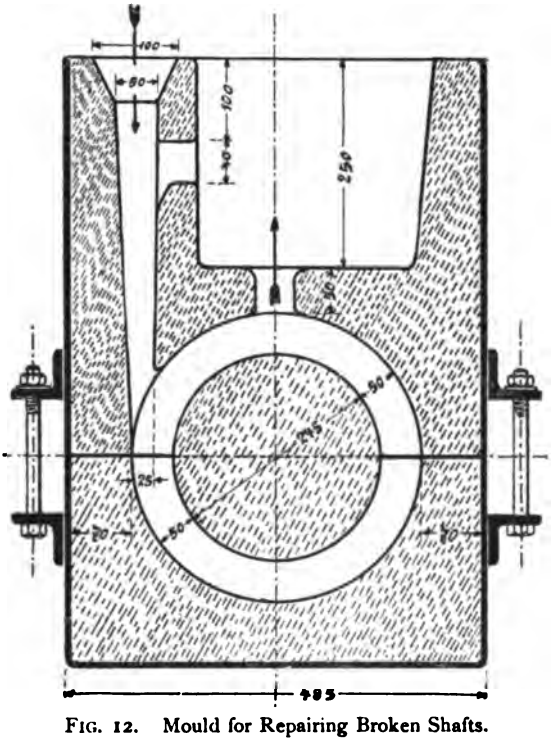


FIG. 12. Mould for Repairing Broken Shafts.

inch of liquid cast iron or cast steel is poured on the welding surface. On this the Thermit powder is poured and ignited. About 30–35 pounds are taken for the superficial foot. This will soften the metal to a depth of about two inches. As soon as the reaction is finished the Thermit must be well stirred. The slag on account of its low specific gravity will thus be driven to the surface and will cling to the iron ring which is suspended in the mould. After a few minutes more liquid steel is added from ladles held in readiness and after thoroughly stirring the contents of the mould the

iron ring is lifted out and all the slag will be found adhering to it. This repair is in common use with the largest works in Germany.

Long cracks or seams can also be welded by a special variation of the process. The liquid steel left in a flat-bottomed crucible after pouring off the slag, is run into the crack and covered by Thermit powder. The latter ignites at once and further increases the already intense heat between and around the crack. I now come to an application of thermit which differs materially from the ones I had the privilege of demonstrating to you up to now. That is welding wrought iron pipes.

FIG. 13. Crank shaft Repaired on Board a Rhine Steamer.

Of course, you will at once object that the heat of the iron must destroy the thin walls of the pipe. That is quite right. But here the corundum slag created on top of the mass in the crucible is what helps me over the difficulty. The slag on being poured has the properties of adhering instantaneously in a thin layer to any object that it comes in contact with, and of being impenetrable to liquid thermit iron. I, therefore, change the sequence of operation and make the slag flow out before the iron. This I do by having the reaction take place in a crucible with a solid bottom from which I pour the contents over the rim.

To butt-weld the pipes they must be made to fit accurately on to each other and must be made bright with a file or emery paper. The two pipes are then closely pressed together by the clamping

apparatus and the sheet-iron mould, well surrounded with moist sand, is attached. After pouring the liquid contents of the crucible, welding temperature will take place within a minute or two. The clamps then want tightening one turn of the screw and

FIG. 14. Welding of a Connecting Rod.

the weld is complete. The mould-box is removed almost at once and can be used several times. The surrounding mass, containing the iron between the layers of slag like the yolk in the white of an egg, is easily removed with a hammer. Such welds

will stand pressures of hundreds of atmospheres, as a matter of fact as much as the pipe itself. About 30,000 to 40,000 pipe joints have been welded by this method, the advantages of which are shortly, that the operation can take place anywhere "in situ," that whole lengths of pipe welded together can be placed in position as one pipe (for instance, where one would have to carry a pipe system across a street), that a welded pipe has no weak points through wear and tear of packing. Its use is therefore imperative in chemical works, for petroleum pipe lines, acetylene gas pipes, etc., etc. Nevertheless, it is cheaper than a solid flange joint. The dimensions of the moulds have been carefully worked out and tab-

FIG. 15. Wrought-Iron Tube Bent at Weld whilst Cold.

ulated for every size of wrought-iron pipe, up to six inches diameter. Any workman will be able to make such welds after very short practice by carefully observing the few rules and directions printed in the pamphlets.

Experiment VII. Pipe Welding. — The numerous other applications of thermit for welding it would take too long to discuss in detail now. But apart from welding there is one large field for which aluminothermics may be of enormus importance. I am referring to foundry practice.

One of my associates, Prof. Mathesius, has specially devoted himself to studies concerning the improvement of iron and steel cast-

ings. These are obtained by introducing the thermit below the surface of the bath and so producing a high temperature in one place. A box containing the thermit is fastened to an iron rod and held down on the bottom of the ladle.

For cast iron and in some cases for steel a special thermit is used which gives off an alloy of iron with titanium so that the

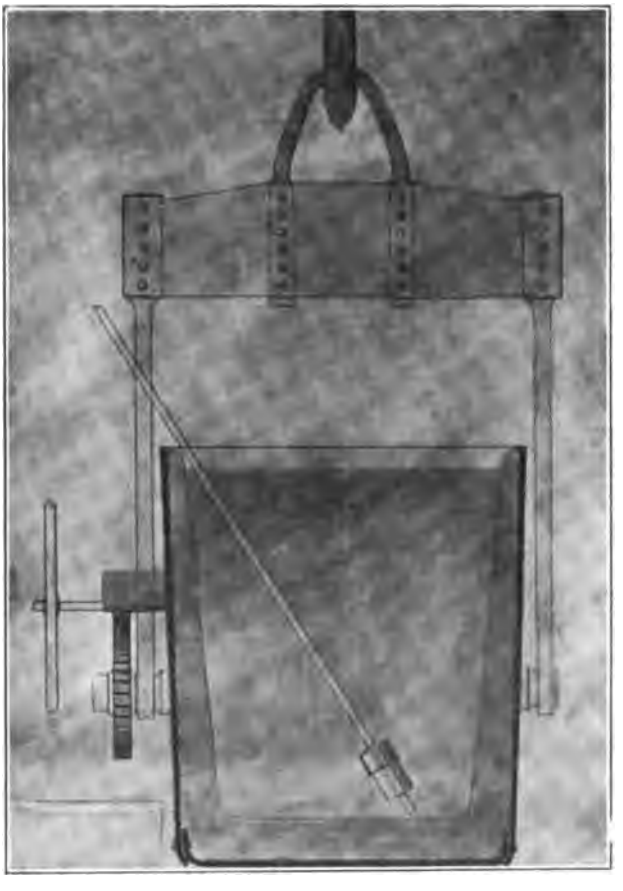


FIG. 16. Shank with Titanium Thermit Box Immersed.

titanium enters the liquid metal. The reaction takes place all through the contents of the ladle and thoroughly stirs them up in the space of a minute or two. Gases and particles of slag are driven upwards so that the fluidity of the iron is increased. An increase of the temperature does not in reality take place, as the

proportion of added thermit is only one quarter to one sixteenth per cent. of the total contents of the ladle. The effect of the titanium is to bind small quantities of nitrogen, to increase the fluidity of the cast iron, and to produce a finer grain.

By such a reaction not only can cast iron be obtained absolutely free from pores, but it is also possible to introduce into the crucible additions of other materials, for instance of ferro-manganese.

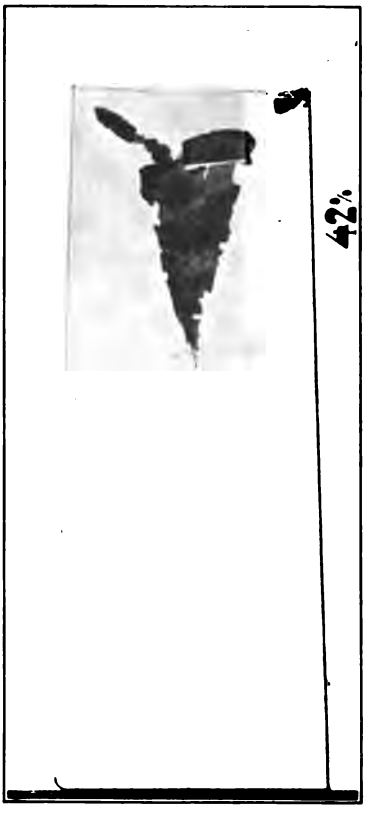


FIG. 17. Steel Block Showing Defective Head (Piping), without Anti-Piping Thermit.

After a so-called "box-reaction" has been carried out, the manganese — which may, for instance, be assumed as 1 per cent. — is found uniformly distributed in the casting. The same method may be used for an addition of nickel for making crucibles used in evaporating caustic alkalis in the chemical industry. In this case, it is better to use the nickel in the form of nickel thermit, which

has been ignited previously in a crucible, and is then poured into the ladle together with the slag. The nickel is then uniformly mixed in by means of a "box-reaction." Nickel-thermit, containing 60 per cent. of metallic nickel, is used in proportion of about 1 per cent. of the contents of the ladle, and with such nickel addition about 50 per cent more charge can be treated than without nickel.

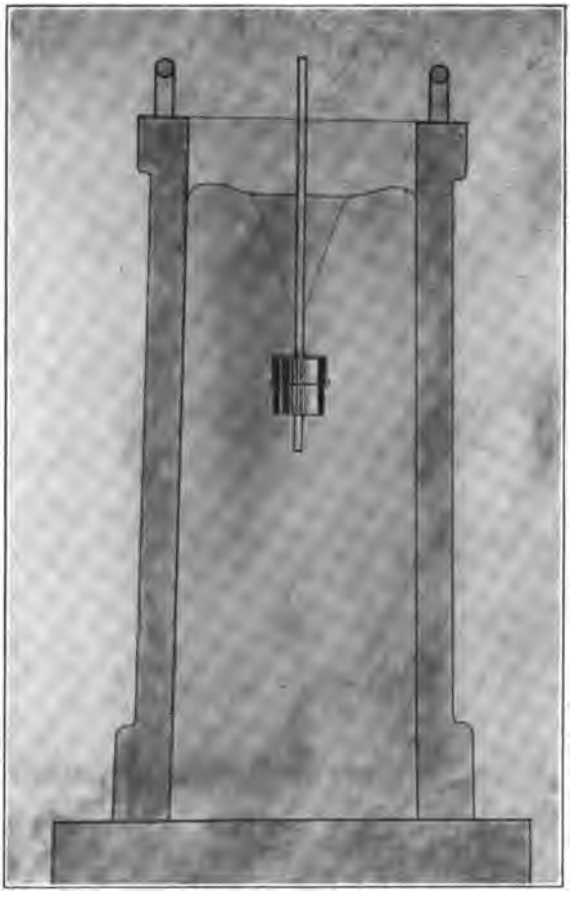


FIG. 18. Steel Block with Box of Anti-Piping Thermit Immersed.

Another application of the so-called "box-reaction" is important for steel castings, and especially for casting large steel ingots, to prevent the familiar phenomenon of piping. In the heads of such blocks hollow spaces are found which mostly cause thirty to forty per cent. of loss.

The thermit process as used for this purpose consists in introducing a box of so-called anti-piping thermit into a block with the aid of an iron rod, in exactly the same way as described before. According to the size of the block the box is suspended about three feet. The reaction is completed in this case in a few seconds. The box is introduced, of course, only after the piping has been formed. The head layer, which has already become solid, is

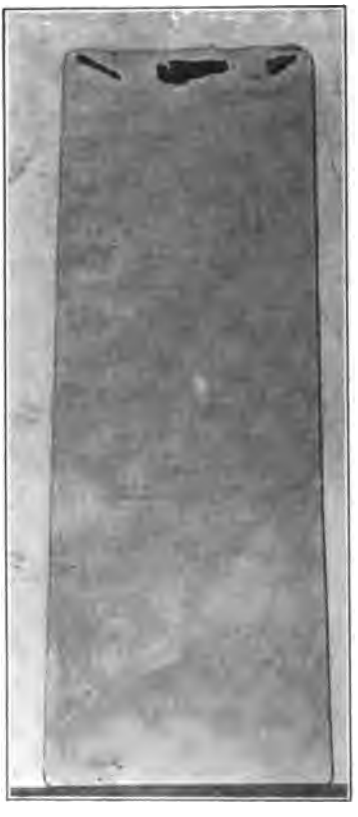


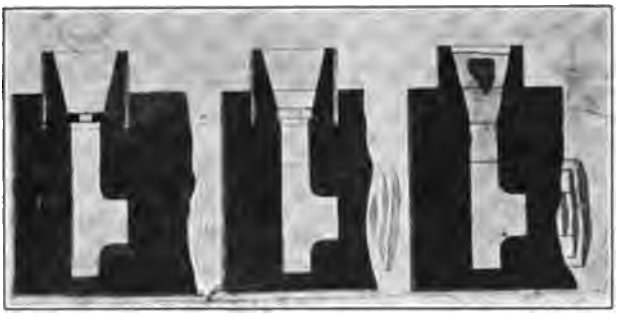
FIG. 19. 10-Ton Steel Block after having been Treated with Anti-Piping Thermit.

broken through for this purpose. Immediately after the reaction is completed, steel, which is held in readiness for this purpose, is poured into the open hole. The method is really very simple, and one learns very quickly at which time to introduce the box. Moreover, the method is very cheap, only about ten pounds of thermit being required for blocks of ten or twenty tons weight. After the

treatment relatively very small flaws were found, and only in the upper part of the block, so that the loss is only a very few per cent.

The method has also been applied for very large steel castings to revive steel which had become plastic in the runners. In this the anti-piping thermit is placed at the bottom of some risers, in an annular box with concentric walls, containing about two and one half pounds of thermit. There is, in this case, no need to thrust the box in by means of an iron rod. The piping will not protrude into the piece, but will be kept right at the head of the riser.

FIG. 20.



Before During After
The Casting.

The difficult operation of casting long stern posts of vessels can be facilitated by inserting in several places boxes of this thermit. On account of the long way steel has to travel it has a tendency to grow plastic. By coming in contact with thermit, its temperature and thereby its fluidity is revived again.

Before concluding I will show you a few lantern slide pictures from photographs of actual work done in all parts of the old world.

1. Complete outfit for railweld.

2. Railwelding at Graz (Austria). The traffic as you see is not interrupted.

3. Railwelding at Berlin (Postdamer Str.); traffic about five cars in a minute. Welds were made a year ago; no breaks have occurred.

4. Railwelding at Ludwigshafen.

5. Railwelding at Leeds.

6. Railwelding at Leeds. The rod held by one of the men is used to keep open the tapping hole after the reaction.

7. Diagram showing arrangement of welding third rail without crucibles.

8. Tube welding on the roof of works.

9. Repairing spokes of wheel of railroad engine, executed by the Austrian State Railway.

10. Ditto, ditto, weld completed.

11. Repairing broken connecting rod; the runner and lost head will have to be knocked off.

12. Welding cast-iron frame of tool machinery in the Transvaal. The broken piece.

13. The same welded.

14. Rhine steamer. Repair of fractured crank shaft of ten inches diameter. Two and one half cwt. of thermit in one reaction. Steamer arrived five P. M. and left next morning at ten.

15. Repair of broken arm of steering-gear on steamship "Assyria," Hamburg-American line. Preparing for the weld.

16. Ditto, ditto, the moment of run.

17. Repair of broken stern-post at Rotterdam. Showing mould-box and crucible.

18. Welded stern-post partly machined.

19. Welding of stern-post of steamer "Sebenico" at Trieste, half part of mould and crucible in position.

20. The same, showing welded piece with half the mould still adhering.

21. Mould completed, but head of riser still adhering. Lost head of runner removed.

22. Broken stern-post of Hamburg-American liner "Sevilla," 9,000 tons. The coke-basket is used for heating one spot so as to facilitate the post being bent back to its original position.

23. Mould and crucible for 7 cwt. of thermit in position.

24. Moment of reaction.

25. Completed weld.

The steamer has repeatedly made the passage to and from Argentine and is registered at Lloyds full class.

ABSTRACTS.

ANALYTICAL CHEMISTRY.

BY E. WALLER.

Lead Peroxide in Analytical Work. St. Bogdan (*Bull. Soc. Chim.* [3] XXIX., No. 12). Excess of H_2S or of $(NH_4)_2S$ may be removed quickly from a solution by adding a little PbO_2 and digesting warm for a short time. The reagent is of great service when it is desirable to remove residual sulphide from a filtrate from precipitation of members of the H_2S group or of the $(NH_4)_2S$ group. As the resultant product is PbS with S which can readily be filtered off, and no Pb goes into solution, this method is very convenient in certain cases. Experiments show that No, Ba, Ca, etc., are retained with the insoluble Pb compounds.

Organic Bases as Reagents for the Separation of Rare Metals. Hartwell (*J. Am. Chem. Soc.*, XXV., 1128). A study of the reaction of a long list of organic bases on salts of Ce, La, Nd, Pr, Th, and Tr in aqueous and partially alcoholic solutions.

Sensitive Indicator. Ossendowsky (*J. Russ. Phys. Chem. Soc.*, XXXV., 845). The purple petals of the Japanese Iris (Kaempferi), after rinsing off with cold water and then digesting in water (in proportion of about 500 cc. water to one pound of the petals), over a water bath for three hours or more, afford a violet solution which constitutes a very sensitive indicator. With mineral acids, bright red; organic acids, crimson red; alkalis, emerald green; organic bases, bright green.

Alkalimetry, etc. Potassium Tetroxalate for Standardizing. Kühling (*Zts. f. angew. Chem.*, XXXVII., 1,031). Crystallize commercial $H_2C_2O_4$, $2H_2O$ twice from HCl (sp. gr. 1.07) and then three times from boiling distilled water. The product should give no precipitate with $AgNO_3$, and leave no residue on ignition. Make a cold saturated solution in water. Titrate one fourth of the solution with concentrated solution of KOH, using phenolphthalein as indicator. Mix in the other three fourths, and stir well. A crystalline precipitate will form. Heat up the solution until it dissolves, then cool and allow to crystallize; pour off the mother liquor, redissolve and recrystallize. Repeat recrystallization again before using the product for standardizing. Allow to dry in the air. The product is KHC_2O_4, $H_2C_2O_4$, $2H_2O$.

Alkalimetry. Material for Standardizing. Lunge (*Zts. angew. Chem.*, XVII., 225). Potassium biniodate KHI_2O_6. The salt is obtained pure only with considerable difficulty. With methyl-orange it is useless. With phenolphthalein one must work in a boiling solution. $Ba(OH)_2$ can be used with this indicator in the cold, but with this it is impossible to make a solution exactly normal or fractional normal.

Potassium tetroxalate, KHC_2O_4, $H_2C_2O_4$, cannot be obtained in necessary condition of purity for a starting point.

Sodium oxalate, $Na_2C_2O_4$, $2H_2O$ (when used ignited to Na_2CO_3). If handled with scrupulous care it is much superior to the two former.

Sodium carbonate, Na_2CO_3. The most certain and most exact (also the cheapest). Without great difficulty a pure salt may be obtained which shows no trace of opalescence (when acidified) with $AgNO_3$ or $BaCl_2$. The presence of possible excess of H_2O or CO_2 is removed by heating to 270° or 300° for twenty or thirty minutes in a platinum dish with constant stirring. The salt should not be allowed to sinter. Cool in a desiccator.

For Iodimetry the biniodate presents no special advantage over pure I.

Ammonia Determination. Riegler (*Zts. Anal. Chem.*, XLII., 677). A gravimetric method is recommended based upon the fact that HIO_3 in excess precipitates from NH_4Cl, $NH_4H_2(IO_3)_2$ insoluble in alcohol. After drying over concentrated H_2SO_4 to constant weight, the prrcipitate contains 3.14 per cent. NH_3.

Potassium Determination. Tarugi (*Soc. Chim. di Roma* through *Chem. Ztg.*, XXVIII., 187). The method is applicable to solutions containing many complex substances such as would be obtained in solution from a fertilizer. It depends on the insolubility of potassium persulphate. To the solution to be tested is added a measured amount of (titrated) $Na_2S_2O_8$ solution in excess; the reaction is:

$$Na_2S_2O_8 + K_2SO_4 = K_2S_2O_8 + Na_2SO_4.$$

After vigorous shaking, this is allowed to stand for three hours, when the precipitate will have settled out in a crust. Addition of a fragment of $K_2S_2O_8$ assists in the formation of the crust. A measured amount of the clear supernatant liquid is then drawn off and titrated. The method for this titration consists in diluting, and then boiling 20 minutes with return cooler to decompose the excess of $Na_2S_2O_8$ to Na_2SO_4, H_2SO_4 and O. Acidimetric titration with phenolphthalein indicator will then serve to show the amount of excess.

Potassium, Colorimetric. Hill (*J. Am. Chem. Soc.* XXV., 990). The K_2PtCl_6 precipitate is dissolved in water (for the standard solution, 0.518 gm. of that salt is dissolved in 100 cc., of which 1 cc. is diluted to 100 for use). The coloration produced by adding 3 cc. of an $SnCl_2$ solution (75 gms. metal in 400 cc.) in the solution tested, and in the standard solutions, are then compared.

Potassium, Chlorimetric. Cameron and Failyer. (*J. Am. Chem. Soc.*, XXV., 1063). The K is precipitated as K_2PtCl_6 (excess of Pt salts removed by alcohol) — dissolved in hot water, a drop of HCl added, and then an excess of KI solution. The color resulting from the reaction of KI with the Pt in solution should be allowed to develop for 4 hours before reading off as compared with standards treated in the same manner. NH_4 salts and organic matter interfere with the test. Addition of alcohol and heating gives a yellow coloration, which may be utilized as a check.

Alkalies in Presence of Borates. Jacobi (*J. Am. Chem. Soc.*, XXVI., 88). Dissolve 2 gms. of the material in HCl — evaporate to dryness and bake for an hour. Filter off SiO_2, precipitate out successively

Fe_2O_3 and Al_2O_3 by ammonia, CaO by (NH_4), C_2O_4, Mg by $(NH_4)_2HPO_4$ and excess of phosphate by Fe_2Cl_6 and NH_4OH. Evaporate the filtrate two or three times with HNO_3 to destroy NH_4 salts. Take up with HCl and evaporate twice to expel HNO_3. Perform the last evaporation in a tared platinum dish, and finally heat gradually up to dull red heat. Cool and weigh. The residue should be B_2O_3, NaCl and $Na_2B_2O_4$. K salts or sulphates if present should be determined in other portions and allowed for in the calculation.

Determine Na_2O in the $Na_2B_2O_4$ by adding methylorange indicator and titrating with $N/_2H_2SO_4$. Then add glycerin in excess, and phenolphthalein indicator, and titrate B_2O_3 with $N/_2KOH$. The sum of the Na_2O and B_2O_3 thus determined subtracted from the weight of mixed salts, gives that of the NaCl. This multiplied by 0.53077 gives the weight of Na_2O to which it corresponds; add to the other result.

In borax free from carbonates, the B_2O^3 can be determined by titration with $N/_2KOH$ with phenolphthalein indicator in a solution containing sufficient glycerin, the burette readings being doubled for calculation, inasmuch as the B_2O_3 is already half combined in the borax.

Free Lime in Cements. Keiser and Forder (*Am. Chem. J.*, XXXI., 153). 0.2 to 0.5 gm. of the cement is weighed out in a platinum crucible, and heated over the blast lamp to expel any CO_2. A few drops of freshly boiled distilled water are then added, and the crucible placed at once inside a "protector" or brass box with screw cover having suitable apertures in sides or top for insertion of a thermometer and of connecting tubes. After heating the protector and crucible in the air bath at 85° for 30 minutes, the temperature is raised to 185° and a slow current of air passed through for 30 minutes. The air passed through is previously deprived of CO_2 and moisture by passing through KOH and $CaCl_2$ tube. From the increase in weight (H_2O) the CaO present is calculated.

Calcium, Conversion of Oxalate to Sulphate. Clark (*J. Am. Chem. Soc.*, XXVI., 110). Bed the platinum crucible containing the precipitate moistened with H_2SO_4 in powdered asbestos placed in a porcelain crucible large enough to receive the platinum-crucible. The full heat of the burner can then be applied and the excess of H_2SO_4 is driven off without spattering.

Alumina, Direct Determination. Barral (*J. Pharm. Chim.*, XIX., 237). A method based on that of Wöhler is recommended. The precipitate of Al_2O_3 and Fe_2O_3 (hydrates) is washed, dissolved in HCl, the solution nearly neutralized with Na_2CO_3, and Na_2SO_3 added until precipitation begins; HCl sufficient to just redissolve is added, and the solution is boiled vigorously. The precipitate consists chiefly of Al_2O_3, by redissolving and repeating the above treatment, practically pure Al_2O_3 may be obtained on igniting the precipitate. Results are accurate within 0.3 per cent. Zn, Mn, Ni and Cu have no influence, TiO_2, P_2O_5, Pb, As or Sb, interfere.

Alumina-Separation from Iron. Leclerc (*C. Rend.*, CXXXVIII., 146). To the dilute solution, slightly acid with H_2SO_4, add $Na_2S_2O_3$ in sufficient amount to reduce iron to ferrous state. Then add large excess of NH_4CHO_2 (formate) and more $Na_2S_2O_3$ and boil. Al is precipitated as basic formate. Fe can be separated from the filtrate as sulphide.

Titanium, Qualitative. Jorrisen (*Bull. Acad. Roy. Belge.*, 1903, 902). Fuse in a bead of $KHSO_4$ until the bead is clear aand does not effervesce. Then crush up the bead and apply 20 to 30 drops concentrated H_2SO_4 containing 0.01 to 0.02 grms. salicylic acid. If Ti is present the fragments are colored red, which color gradually spreads into the solution. The test is not applicable in presence of Vd, Mo or W.

Separation of Manganese and Iron. Dittrich (*Ber.*, XXXVI., 2330). Having the solution in a small bulk of water, add a few drops of H_2SO_4, heat, and add crystals of Na_2SO_3 until decolorization and the odor of SO_2 persists. Then add in concentrated solution 4 gms. pure KCN, and 1 gm. Na_2SO_3 and heat again. Ferrocyanide and manganocyanide are formed. At this point the addition of 0.5 gm. NaOH will decompose the manganocyanide affording Mn $(OH)_2$ while the ferrocyanide is unaltered. Addition of 20 to 30 cc. of three per cent. H_2O_2 will completely separate the Mn as hydrated MnO_2.

Zinc Determination. Herting (*Chem. Ztg.*, XXVII., 986). The method of Murman (Analyst, XXIV., 51) is commended. This consists in adding a little $HgCl_2$ to the solution previous to precipitating by H_2S. Filtration may be more readily effected and the precipitate on ignition yields all the Zn as ZnO, the Hg compounds volatilizing without carrying off any Zn. Zn can easily be separated from Fe(ic) by two precipitations with NH_4OH, if each time a little $NH_4C_2H_3O_2$ is present in the solution.

Zinc-Ferrocyanide Method. Waring (*J. Am. Chem. Soc.*, XXVI., 4). The author presents a careful study of the possible sources of error in the estimation of Zn by this method. Among other points is noted that in dehydrating the mass obtained by dissolving a Zn ore in HCl or aqua regia and evaporating, heating to 145° C. or above, will volatilize considerable amounts of $ZnCl_2$. Some ores contain zinc spinels, which can only be decomposed by fusion with soda in presence of SiO_2 or borax.

The occlusion of ZnO by hydrated SiO_2, Fe_2O_3 or Al_2O_3 when ammonia is added, will amount to negligible quantities, if the precipitate is redissolved and reprecipitated a couple of times. Manganese if present, should be preferably separated by use of persulphate and Br water.

For umpire and control analyses it is preferable to separate the Zn by H_2S.

The method given for all classes of zinc ores, consists in attacking an amount of the sample estimated to contain 0.2 to 0.3 gm. Zn with HCl or aqua regia, subsequently evaporating with HCl or H_2SO_4 to remove all nitrous compounds. If zinc spinels are present the residue should be fused as previously suggested. Evaporation to absolute dryness is not necessary. The filtrate and washings are then boiled for 15 or 20 minutes with a strip of clean sheet iron or steel. This will remove Cu and all other metals likely to interfere except Cd. The use of metallic Al (which would also remove Cd) has been suggested, but apparently the author has not tried it. Neutralize very closely with dilute NaOH until just permanently cloudy, then render just acid with formic acid, and add about 0.5 cc. more (50 per cent. $HCHO_2$). Dilute to 200 to 250 cc. and heat to about 80° C. Pass in a rapid current of H_2S. By this means a granular precipitate which is easily filtered and washed with hot

water is obtained. Spread the filter with contents on the inner wall of a capacious beaker, and wash off with a jet of hot water.

Use 10 cc. conc. HCl to rinse out the precipitating flask and gas delivery tube, and pour it (diluted with water) over the paper as well. The yellow of CdS will be perceived at this point if Cd is present, in which case H_2S water must be added, allowed to settle, and the CdS filtered off. The Zn solution is made up to 200–250 cc.; heated to 60°, a little NH_4Cl added; and it may be then titrated. Minute directions are given regarding the management of the titration for standardizing, and for analysis.

Incidentally the author finds that much of the so-called C.P.Zn and ZnO are very impure.

The standard solution of ferrocyanide for 1 cc. = 0.005 gm. Zn requires theoretically 21.544 gms. $K_4FeCy_6 \cdot 3H_2O$ per liter. On account of the inevitable impurities the amount recommended is given as 21.63 gms. The addition of 7 gms. Na_2SO_3 crystals is recommended to neutralize the effects in some cases of residual oxidizing reagents which may have been used. It also preserves the reagent.

Commercial Nickel. (*Holland Bull. Soc. Chim.*, XXIX., 1073). Impurities; Cu, Co, Fe, Al, Ca, Mg, S, Si, C, As, Sb. Weigh out 5 gms. of the sample in a deep beaker, add 25 cc. HNO_3 and 25 cc. H_2O, cover with a funnel. Heat gently — finally to ebullition. Remove from the heat. Allow to stand 15 minutes, then add 10 cc. H_2SO_4 and evaporate to copious fumes. Cool, take up with water. Add NH_4OH (2 or 3 cc. in excess), boil for a few moments then add 25 cc. NH_4OH, and a few cc. of H_2O_2. Dilute to 300 cc. and electrolyze at about 90° with a current of 1 amp. depositing on platinum gauze. When all the Ni has been deposited, filter off the precipitated $Fe_2(OH)_6$, insoluble SiO_2, etc., dissolve in H_2SO_4, add NH_4OH in excess to the solution, unite with the original solution, and electrolyze again to recover traces of Ni, Co and Cu. Wash with water, then with alcohol, dry and weigh.

For Cu, dissolve the deposited metal in 50 cc. HNO_3 (at 36°) diluted with 50 cc. H_2O. Dilute to 300 cc. and electrolyze with a current of 1 amp. For Co, evaporate the solution from which the Cu has been removed to a syrup, take up with water, render alkaline with KOH, then acid with acetic, and precipitate out Co by KNO_2. Dissolve the precipitate in H_2SO_4 with a little HCl, evaporate to fumes, dilute and electrolyze as before.

Iron. Dissolve the precipitate produced by NH_4OH, in dilute H_2SO_4. Precipitate out Sb and As by H_2S. Filter those out, heat to expel H_2S, and then add 5 gms. citric acid 25 to 50 cc. of SO_2 solution, 25 cc. NH_4OH and finally H_2SO_4 drop by drop until the solution is neutral. Add a few cc. NH_4OH, dilute to 300 cc. and electrolyze at about 40° with a 1 ampere current. The Fe deposits in a short time; as it contains a little C and some of the Pt from the anode, it is better to determine it volumetrically by dissolving off with H_2SO_4 and titrating with permanganate.

For Al, etc., evaporate the solution from the Fe to dryness with excess of H_2SO_4. To destroy the organic acids take up with H_2SO_4 and HNO_3 and evaporate again. Dissolve finally in dilute HCl, and precipitate out $Al_2(OH)_6$ by NH_4OH. In the filtrate determine Ca and Mg.

For S and Si. Dissolve 5 to 10 gms. of the sample in HNO_3 (1 : 1), add 25 cc. HCl and evaporate on the water-bath. Repeat evaporation with HCl until no nitrate remains. Filter off the SiO_2 (which still contains some of the S). Saturate the filter paper with NH_4NO_3, burn, and fuse with 2 gms. Na_2CO_3, cool, dissolve the mass in dilute HCl, evaporate to dryness to separate SiO_2, filter, and in the combined solutions separate S (now as sulphate) by $BaCl_2$.

C is determined as in Steels.

As, by distilling a mixture of $FeSO_4$ and HCl in contact with a weighed portion of the metallic sample.

For Sb. To the solution from which As has been removed, add $ZnCl_2$ and distil in a current of gaseous HCl. Precipitate the distillate with H_2S, and determine electrolytically.

Arsenic and Antimony in Nickel Speiss. Nissenson and Mittasch (*Chem. Ztg.*, XXVIII., 184). Györy's method, modified titration with $KBrO_3$, using indigo solution as indicator, is the one applied. 0.5 gm. of well-pulverized speiss are treated in an Erlenmeyer flask with 8 cc. conc. H_2SO_4, digesting at 300° to 400° on the sand bath, until the solid mass has become white or nearly so. This may require some hours. After cooling, add 50 to 100 cc. water and heat to boiling for some little time to bring the basic salts into solution and without filtering, pass in H_2S. Filter off the precipitate, after settling, and wash with acidified water containing H_2S. Rinse the sulphides back into the flask, with water or dilute H_2SO_4, and add 7 cc. conc. H_2SO_4. Then heat on the sand bath until the Sb and As dissolve in the triad condition. At a certain stage a metallic sponge appears in the mass, which must be removed by further heating before the next step is taken. When the sulphides are completely dissolved (leaving silica and gangue, etc.), cool, add about 100 cc. water, heat strongly and titrate with N/10 $KBrO_3$, using three drops of solution of indigo in H_2SO_4 as indicator. If the proportion of Sb and As is approximately known, the indicator need not be added until a considerable proportion of the standard $KBrO_3$ has been added. If, however, that is not the case, and the indicator is added at the start, more indicator will have to be added later on, as it is slowly destroyed by the conditions produced. The result shows Sb and As together. The As can be separated by adding more $KBrO_3$, evaporating somewhat, and after cooling adding one half to one gm. tartaric, then ammonia in excess, and magnesia mixture. After standing some time cold, filter off $MgNH_4AsO_4$, acidify the filtrate precipitate Sb by H_2S, dissolve that precipitate in H_2SO_4 and titrate.

Antimony in Commercial Lead. Nissenson and Siedler. (*Chem. Ztg.*, XXVII., 749). Subdivide as finely as possible and treat 1 gm. with 20 cc. saturated Br water with HCl, with constant agitation, warming gently at the same time. Too high a heat wastes the Br to no purpose. When all metal has disappeared completely, boil until the vapors show but little color of Br. Cool, and add a few small crystals of Na_2SO_3 in two or three successive portions. Boil out the SO_2, add 20 cc. KCl and boil again, to insure getting the Sb in the *ous* form, and titrate hot with N/10 $KBrO_3$ (2.7852 gms. pure crystals per liter). Methyl-orange may be used as indicator, but sulphindigotic acid is preferable. The indicator should not be added until near the end of the titration. Fe and Cu up to 0.5 per

cent. do not interfere with this titration. Nor do S or undissolved sulphides in case the method is applied to ores.

Separation of Tin and Antimony. Henz. (*Zts. Anorg. Chem.*, XXXVII., 1). The author modifies Clarke's oxalic method by oxidizing the sulphide solution with H_2O_2 and then proceeding. Place the sulphide solution (in small bulk), which should not contain over 0.3 gm. of the alloy, in a 500 cc. beaker. Add 6 gms. pure KOH and 3 gms. $H_2C_4H_4O_6$, then twice as much 30 per cent. H_2O_2 as suffices to decolorize. Boil a few minutes, cool somewhat and add a hot solution of 15 gms. $H_2C_2O_4$. The volume of the liquid should now be 80 to 100 cc. Boil hard 10 minutes and then begin to pass in H_2S, keeping up the boiling 15 minutes after the Sb begins to come down. Dilute to 250 cc. with boiling water. Boil 15 minutes longer, then remove the lamp and continue passing H_2S for 10 minutes more. Filter on a Gooch crucible and wash twice with a 1 per cent. solution of $H_2C_2O_4$, then with dilute $HC_2H_3O_2$. The washing liquids should be boiling hot and saturated with H_2S.

Place the Gooch in a wide tube through which is passed CO_2. Heat first to 100°–130° to expel moisture, then finally to 500°. Weigh as Sb_2S_3.

The Sn in the filtrate is determined by evaporating to small bulk and electrolyzing at 60° to 80° with a current of 0.2–0.3 ampere and 2–3 volt. After six hours add 5 cc. H_2SO_4 (1:1) and continue electrolyzing for 18 hours. Results for Sn usually run a little low.

Gold, Iodometric Determination. Maxson (*Zts. Anorg. Chem.*, XXXVII., 801). Gooch and Morley's method (*Am. J. Sci.*, VIII., 261) depends on the reaction

$$3\,KI + AuCl_3 = 3KCl + AuI + I_2$$

being managed in many respects similar to the iodide method for Cu. Rupp's method (*Ber.*, XXXV., 2,011) with As_2O_3 depends on the reaction

$$3As_2O_3 + 4AuCl_3 + 6H_2O = 3As_2O_5 + 12HCl + 4Au.$$

The excess of As_2O_3 is titrated with standard I solution. The first named method is decidedly the more accurate.

Analysis of Iridosmine. Leidie and Quennessen (*Bull. Soc. Chim.*, XXIX., 801). The material is first brought to a condition of subdivision by fusion with zinc, and then volatilizing off the Zn. Then the material is brought into soluble form by use of materials in the following proportions: Fuse 10 gms. NaOH in a nickel capsule, and project into it little by little a mixture of 10 gms. of the subdivided iridosmine intimately mixed with 40 gms. Na_2O_2. Stir frequently with a nickel spatula and keep a heat sufficient to maintain the mass in a semi-fluid condition. The operation should occupy about half an hour. The use of NaOH lowers the fusion temperature of the Na_2O_2 and diminishes the attack of the crucible. Pour out upon a nickel plate. When cool break up and project in small portions into a liter of water in a porcelain dish covered with a funnel. Cool the solution, let settle, decant and take up the insoluble residue with diluted NaClO, to dissolve the RuO_2. Unite the solutions. The solution is placed in a tubulated retort delivering into a

glass balloon receiver, with lateral and central tubulures which in turn delivers into a second and a third balloon, the connections being made with ground joints. All three should be plunged in a refrigerating mixture. Cl is then passed in — at first in the cold; afterward when bubbles of oxygen are given off the retort is heated to 70°. OsO_4 and RuO_4 are volatilized and condensed in the balloons, leaving Ir_2O_6 in the retort. The contents of the retort should remain alkaline throughout.

The condensed solutions are then placed in a retort connected with three receivers arranged in a similar manner to those already described, and like them immersed in a refrigerating mixture. The first receiver is half filled with HCl, to collect the Ru as Ru_2Cl_6. The second and third contain 12 per cent. NaOH and 2 per cent. alcohol to take up Os as Na_2OsO_4. Heat to 70° and pass a slow current of air. When about half of the contents of the retort have been distilled over, the distillate should show no blackening with H_2S and the operation is finished. The contents of the retort containing the iridium is acidulated with HCl and any residue is dissolved in dilute HCl. If any insoluble iridosmine remains, separate and deduct from the amount originally taken. Heat the solution, and add $NaNO_2$, followed by Na_2CO_3. On filtering, one obtains a solution of sodium iridium nitrite.

Precipitate the NaOH solution of Os by strips of metallic Al. Evaporate the Ru solution to a syrup and precipitate by metallic Mg. The Ir solution is treated essentially in the same manner. In this case, after evaporating off all excess of acid, it may be more convenient to dilute to some known bulk, and use an aliquot portion for precipitation by metallic Mg.

Decomposition of Galena and Chalcopyrite. Boucher (*Bull. Soc. Chim.*, XXIX., No. 18). A very efficient agent has been found in a mixture of three parts sodium persulphate with one part NH_4NO_3. One to 2 gms. of the finely pulverized mineral is mixed intimately with 4 to 5 gms. of the above mixture and heated for five or six minutes on a moderately heated sand bath, applying the heat rather moderately at the beginning. Galenas may be subjected to the treatment in an iron or capacious porcelain crucible. Chalcopyrite had best be attacked in a Kjeldahl matras of Jena glass, as the action is more violent, and the form of the flask will prevent losses. After the heating the mass should show no blackish grains of undecomposed mineral, though in some cases Mn may show black MnO_2 or there may be some unattacked gangue of dark color.

After the fusion, treatment with water will afford insoluble $PbSO_4$ gangue, etc., and a sulphate solution of the other metals. Blende, stibnite, mispickel, etc., did not give satisfactory results with the method, the attack being incomplete.

Commercial Lead. Soft Lead. Herting (*Chem. Ztg.*, XXVII., 923). For high-grade leads 200 gms. is too small an amount to be used for the determination of impurities; 400 to 500 gms. are necessary. The solid material deposited after dissolving never contains lead antimoniate. That compound is insoluble in HCl, and has a yellow color. Any Sb_2O_4 remaining in the residue will be dissolved out by HCl and tartaric.

After removing most of the Pb from the solution as $PbSO_4$, H_2S is

passed in, and the precipitate dissolved in HNO_3, and the solution treated with considerable excess of H_2SO_4 to retain the Bi. NH_4OH in excess (not the carbonate) is added to separate Bi, leaving CuCd and Ag in solution. The Biprecipitate must be washed with warm NH_4OH, redissolved and precipitated for weighing by $(NH_4)_2CO_3$. Ag is separated out by HCl, and Cu and Cd are separated by treatment with H_2S and $1:5H_2SO_4$. Bi if present in proportion of 0.02 per cent. is objectionable.

Silver Cyanide. Plummer (*Proc. Lond. Chem. Soc.*, XIX., 285). When freshly precipitated, AgCN will dissolve in boiling dilute HNO_3, though insoluble in cold. HCN is evolved which can be passed over into $AgNO_3$ solution and thus estimated in case a separation from AgCl is required. After drying the AgCN aggregates in hard lumps which offer greater resistance to the solvent, and some oxidation of the HCN may occur.

Colorimetric for Bismuth. Planès (*J. Pharm. Chim.*, [6], XVIII. No. 9). KI added to a solution of Bi gives a brown precipitate, unless the KI is in excess, in which case an orange-yellow solution is obtained. If the solution contains an equal volume of glycerin (at 30°) no precipitate is formed, whatever the relative proportions of the salts. The coloration is most intense when 6KI are present to one atom of Bl. 996 : 208 or 4.79 gms KI to 1 gm. Bi.

The standard solution of Bi is made to contain 1 gm. Bi in 100 cc. After dissolving the Bi in HNO_3 with a little water, the dilution is made with glycerin of the above strength. The KI solution (5 per cent.) is made up in a similar manner. The Bi in a substance to be tested is brought into solution which is made up to 100 cc. or some convenient bulk, and an amount of the standard solution containing approximately the same amount of Bi is made up to the same bulk, using, in both cases, enough glycerin to make the proportion such as is given above; KI solution is added, in proportion to the amount of standard Bi solution used, and the colors are compared, either by varying the depth of the liquids or by dilution.

Bismuth Estimation. Rupp and Schaumann (*Zts. Anorg. Chem.*, XXXII, 359). The Bi solution, as nearly neutral as it can be made without precipitating, is poured into a known amount of standard solution of $K_2Cr_2O_7$ (about 5 per cent.). Then dilute, shake vigorously, and filter after ten minutes on a dry filter. In an aliquot portion of the filtrate determine the excess of CrO_3 remaining by adding KI and H_2SO_4 and titrating with standard $Na_2S_2O_3$.

Separating Tellurium from Antimony. Gutbier (*Zts. Anorg. Chem.*, XXXII., 260). An HCl solution free from sulphates and nitrates should be used. Then on adding a large excess of tartaric acid, followed by hydrazine hydrate Te is separated out. In the filtrate Sb may be separated by H_2S, etc.

In a strongly ammoniacal solution addition of large excess of tartaric acid followed by solid hydroxylamine hydrochlorate, will also effect separation of Te, but the method is less rapidly carried through.

Selenium and Tellurium Separation. Pellini (*Gaz. Chim. Ital.*, XXX., 1, 515). To the solution of SeO_2 and TeO_2 (0.1 to 0.5 gm.) slightly

acid with HCl, is added 50 to 100 cc. of saturated solution of $(NH_4)_2\,C_4H_4O_6$ and hydrazine, sulphate when the mixture is heated for one to two hours. Se only is precipitated. In the filtrate Te is precipitated by H_2S, oxidized with fuming HNO_3, finally reduced to elemental form by hydrazine hydrochloride, etc.

Selenium Estimation. Pellini and Spelta (*Gaz. Chim. Ital.*, XXXIII., 89). Hydrazine with SeO_2 reacts thus:

$$N_2H_4 + SeO_2 = Se + 2H_2O + N_2.$$

The Se may be estimated by measuring the N evolved in a modified Schultze-Tiemann apparatus.

The SeO_2 in water or very dilute HCl, is placed in the flask, and the volume brought up to 50 cc., some NaCl is added and air is boiled out of the solution. One then adds a solution of 2 gms. hydrazine hydrochloride or sulphate acidulated with HCl, which has been previously boiled. The evolution of N occurs promptly and stops abruptly. The method is specially applicable for small amounts as 1 gm. SeO_2 would afford 201.83 cc. N.

Te gives a slow and indefinitely prolonged evolution of N, so the reaction is unsuited for the estimation of that element.

Cerium Separation. Boehm (*Zts. angew. Chem.*, XVI., 1129). In presence of NaOH, ClO_2 is precipitated by $K_2Mn_2O_8$. Excess of the permanganate is best avoided. The precipitate after washing with water should be treated with HNO_3 of 10 to 20 per cent., which will dissolve off any of the other earths that may be with the precipitate. From the resulting mixture of CeO_2 and MnO_2 the former may be dissolved out by stronger mineral acids.

Determination of Vanadium. Campagne (*C. Rend.*, XXXVII., 570), $VOCl_3$ by prolonged boiling with HCl is reduced to $VOCl_2$, whereas Fe_2Cl_6 is not affected. Addition of H_2SO_4 then affords blue $V_2O_2(SO_4)_2$, which by titration with permanganate is oxidized to $V_2O_2(SO_4)_3$. If the method is applied to steels, etc., the major part of the Fe_2Cl_6 should be separated with ether in presence of strong HCl.

Chlorates, Bromates and Iodates. Debourdeaux (*C. Rend.*, CXXXVIII., 147). A solution made up to contain 5 gms. $MnSO_4$ and 12 cc. conc. H_2SO_4 in 100 cc., when slowly heated up to boiling with $H_2C_2O_4$ and a chlorate or bromate affords quantitatively CO_2 and HCl or HBr, with iodidate it gives CO_2 and free I. By using known amounts of a standard solution of $H_2C_2O_4$, and afterward titrating back with standard $K_2Mn_2O_8$ solution, the amounts of these substances can be determined. The halogen acids remaining should be removed by precipitation with $AgNO_3$ before proceeding to the latter titration.

$$HClO_3 + 3H_2C_2O_4 = 6CO_2 + 3H_2O + HCl$$

Similarly for $HBrO_3$. Also:

$$HIO_3 + 5H_2C_2O_4 = 10CO_2 + 6H_2O + I_2$$

Determining Chlorine in Presence of Carbon Dioxide, especially in the case of electrolytic Cl. Schlötter (*Zts. f. angew. Chem.*, XVII., 301). The determination can be made eudiometrically. Hydrazine salts react

with free halogens after this fashion: $N_2H_4 + 2Cl_2 = 4HCl + N_2$ or, two volumes of Cl correspond to one volume of N. By using a Bunte burette and taking a convenient volume of the mixed gases (100 cc.), then running in hydrazin sulphate and shaking vigorously, and afterward adding more of the hydrazin salt and shaking until the gas volume shows no perceptible diminution, the diminution in volume multiplied by two gives the volume of Cl. In determining the CO_2 afterward, the most of the hydrazin salt had best be removed, since it decomposes in presence carbonates or bicarbonates.

Bromates, Estimation. Schlötter (*Zts. Anorg. Chem.*, XXXVII., 172). Alkaline bromates react thus with hydrazine:

$$2NaBrO_3 + 3N_2H_4 = 2NaBr + 6H_2O + 6N.$$

By measuring the N evolved, the amount of bromate may be estimated. The apparatus consists of two 200 cc. flasks, each carrying a two hole cork with connecting tubes, and an eudiometer tube. The first receives a charge of hydrazine-sulphate three times the weight of the bromate tested. One tube is a vent and terminates just below the cork, the other tube dips to the bottom, and is bent over to be connected by a short piece of rubber tubing (with pinch cock) with the tube of the second flask. The other tube from the second flask leads into a water trough for delivery of the N. A rubber tube connection (with pinch cock) is also on the delivery tube. Both flasks are about two thirds filled with water in which the salts are dissolved, and the contents of both flasks are boiled down to 30 or 40 cc. to expel all air. Toward the end of the boiling the connection tube is closed that the steam may drive out all air in the delivery tube. When this is accomplished the delivery tube is closed, and the connection tube opened. Then on cooling, the hydrazine solution is drawn over upon the the bromate solution, the eudiometer is put in place and the delivery tube opened. Then close the connection tube and heat the second flask until no more gas is evolved. The N obtained is measured, and its weight calculated.

Iodides, Action of Boric Acid. Baubigny and Rivals (*C. Rend.*, CXXXVII., 650). H_3BO_3 displaces HI from iodides in the cold, but is without action on chlorides or bromides, whether in hot or cold solution, unless the solution is very concentrated. Addition of $MnO_2.H_2O$. sets free I under these conditions. Care must be exercised to avo.d using too much of the hydrated MnO_2. which might then form iodates.

Sulphuric Acid Determination. Silberberger (*Ber.*, XXXVI., 2758). The difficulties of determination as $BaSO_4$, in presence of Fe, Al, Cr. etc., are obviated by precipitation with $SrCl_2$ in alcoholic solution, *e. g.*, in pyrites. Treat 0.5 gm. with 20 cc. aqua regia, evaporate several times with HCl, treat the residue with hot HCl and filter. Then add alcoholic solution of $SrCl_2$ and 100 cc. acohol. Digest one hour and decant the clear solution through a filter. Stir the precipitate with 2 cc. HCl and 50 cc. alcohol, settle, decant, wash three times with alcohol by decantation, and finally on the filter. Results somewhat higher than by Lunge's or Kuster's method are thus obtained.

Estimating Persulphates. Marie and Bunel (*Bull. Soc. Chim.* [3], XXIX., No. 18). Dissolve 0.3 to 0.4 gm. in 100 cc. wa·er; neutralize

in presence of methylorange, then add 2 cc. methylalcohol, heat five minutes to 70–80°, then boil ten minutes, cool, and titrate with decinormal NaOH, methylorange indicator. It has been proved by the authors that no formic acid is formed under these conditions.

Sulphur in Coal and Coke (rapid method). Pennock and Morton (*J. Am Chem. Soc.*, XXV., 1265). The method consists in mixing the fuel with Na_2O_2, firing by insertion of a red-hot wire, dissolving in water, adding HCl solution of $BaCrO_4$, rendering aikaline, filtering off mixed $BaSO_4$ and $BaCrO_4$, and titrating the chromate which has been displaced by sulphate with standard $Na_2S_2O_3$.

The apparatus consists of soft steel crucible (about 40 cc. capacity), with a hole in the cover through which to insert the hot wire. A support for it is made by a sheet of aluminum in which points have been cut, some turned upward, some turned downward, to raise the crucible clear of the bottom of the beaker in which the firing is done.

The reagents are: $BaCrO_4$ solution: 23 gms. in 80 cc. conc. HCl and 980 cc. water. The material is best made in the laboratory. That purchased from dealers is often impure.

$Na_2S_2O_3$ solution. Tenth normal. 24.8 gms. crystals in 1 liter.

I solution. Tenth normal. 12.69 gms. I with 18 gms. KI dissolved in 50 cc. H_2O and diluted to 1 liter.

Starch solution. With 0.7 gms. of the fuel mix thoroughly 16 gms. Na_2O_2 for coal, or with 11.5 gms. for coke, in the crucible. Cover, place the crucible on its stand in a 20-ounce beaker containing enough water to half immerse the crucible. Ignite by means of a red-hot wire. After three to five minutes remove the stand and tip the crucible on its side to soak out the charge. Remove and rinse off the crucible, add HCl to acidity and boil. Then, while still boiling, add a slight excess of ammonia, then 15 cc. of the $BaCrO_4$ solution and boil for a minute. Add water to make the solution up to 200 cc., then ammonia in decided excess, and boil a couple of minutes longer. Allow to settle and then filter, washing twice with 20 to 30 cc. water each time.

To the filtrate add about 1 gm. KI, cool to 30° C, add 5 cc. HCl, and titrate with $N/10 Na_2S_2C_3$ solution finishing with starch indicator. If necessary titrate back with N/10I solution.

Two or three analyses can be accomplished in an hour by this method.

The proportion of Na_2C_2 used must be regulated with some care. If too small in amount the ignition will be too violent. If too large the combustion will be incomplete.

Gravimetric Determination of Phosphoric Acid and Magnesia. Molybdic method. Reigler, *Zts. Anal. Chem.*, XLI., 675). Addition of $BaCl_2$ to NH_4OH solution of phospho-molybdate (yellow precipitate) affords a precipitate of $Ba_{27}(MoO_4)_{24}P_2O_8.24H_2O$. The high molecular weight of this precipitate, permits the very exact determination of very small amounts of P_2O_5.

Magnesia may be determined by precipitating as phosphate in the usual manner, converting to phospho-molybdate, and treating as above suggested. This method is specially applicable for determination of MgO in potable waters.

Ferro Silicon. Lidholm (*Zts. angew. Chem.*, XVI., 1030). Fuse 0.3 gm. of the sample with 15 times its weight of 1 part K_2CO_3 and 2

parts Na_2O_2 in a nickel crucible. Dissolve in water, acidify with HCl, evaporate to dryness, etc

The process serves for the estimation of S also, though in that case, a larger amount of the sample should be taken.

Boric Acid in Presence of Stronger Acids. Herz (*Zts. Anorg. Chem.*, XXXIII., 353). By use of nitrophenol as indicator, the stronger acid HCl, H_2SO_4, etc., may be titrated with standard alkali, then on addition of mannite or glycerin, and phenolphthalein indicator, the B_2O_3 may be titrated.

Boric Acid Determination. Mylius and Meusser. (*Ber.*, XXXVII., 397). Mixtures of H_3BO_3 and H_3PO_4 give no precipitate in aqueous solutions. In conc. H_2SO_4 or in glacial acetic acid, they unite to form H_2BOPO_4 which by ignition affords BPO_4, which is nonvolatile. Addition of water decomposes this to H_3BO_3 and H_3PO_4. By adding acid and alcohol to a solution and distilling, all the H_3BoO_3 can be obtained in the distillate. To this, addition of H_3PO_4 followed by excess of NH_4OH, and evaporating, and finally igniting at 400° in a current of steam the BPO_4 corresponding to H_3BO_3 present is obtained. The method is accurate to within about 1 per cent. of the B_2O_3 present.

Free Carbonic Acid in Water. McGill (*Jour. Chem. Soc.*, XXVI., 183). The test should be performed on the spot. In most cases 500 cc, is a convenient quantity of the water to take for testing. This is placed in a bottle with suitable connections which contains about one ounce of glass beads (solid). The rubber connecting tubes are long enough to permit frequent shaking. Air (deprived of CO_2 by passing through soda lime) is forced through the sample into "absorbers," consisting of phials 7 inches high by 1¼ inches diameter, filled with glass beads. The inlet tube passes to the bottom, the outlet tube terminates just below the cork. 10 cc. of N/100 $Ba(OH)_2$ solution is added to each absorber, of which three or four may be used. Addition of phenolphthalein to the sample will serve to show by the coloration when decomposition of bicarbonates begins, which will not happen if the air is passed in slowly. About five bubbles per second is a suitable rate.

Addition of phenolphthalein to the absorbers will also indicate (by loss of color) approximately the proportion of free CO_2 in the sample. The exact amount can be determined by titrating back. For the air supply, an india rubber bag, inflated by a bicycle pump, will answer.

Reaction of Nitrites. Blunt (*Analyst.*, XXVIII., 313). A sample of water containing nitrites when tested with ferrocyanide (Fe being suspected) gave at once the yellow coloration due to ferricyanide. The reaction seems to be delicate.

Nitric Acid in Nitrates, Volumetric. Debordeaux (*Bull. Soc. Chim.*, XXX1., 3). The author finds that $H_2C_2O_4$ alone is not decomposed by boiling with H_2SO_4 containing 20 cc. (conc. H_2SO_4) per 100 cc. In presence of nitrate there is also hardly any action. If $MnSO_4$ is introduced besides, decomposition will take place. If the H_2SO_4 is 20 per cent. or over by volume the product is NO. If less than that (12 to 14 per cent.) the product is N_2O

$$4H_2C_2O_4.2H_2O + 2KNO_3 + H_2SO_4 = 13H_2O + K_2SO_4 + 8CO_2 + N_2O.$$

On these facts is based the process proposed.

A standard solution of $K_2Mn_2O_8$ is prepared containing about 20 gms. per liter, which is standardized by pure recrystallized $H_2C_2O_4.2H_2O$. This is used to titrate the oxalic solution before and after the operation on a weighed quantity of the material. The difference between the two titrations affords the basis for calculation.

The oxalic solution should contain per liter:

Cryst oxalic acid $H_2C_2O_4.2H_2O$,	35 to 40 gms.
Cryst manganese sulphate $MnSO_27H_2O$,	50 gms.
Concentrated H_2SO_4.	120 cc.

Weigh out 0.3 to 0.5 gm. of the sample, in a small flask, add 50 cc. of the oxalic solution, adapt to the flask a reversed condenser, immerse the flask in the water of a water-bath at the ordinary temperature, apply heat to the water-bath and gradually (in about 30 minutes) bring the water to boiling. By this time all evolution of gas should have ceased, and the contents of the flask may be titrated back with the standard $K_2Mn_2O_8$ solution.

Portland Cement Distinguished from Slag Cement. Seger & Cramer (*Chem. Ztg.*, XXVII., 879). Pass the material through a 100 mesh sieve and boil 50 gms. with 100 cc. of water for three hours, keeping up the volume of water by additions from time to time, and agitating occasionally to prevent formation of lumps. Filter, wash twice with hot water, and dry at 100 to 120°. In 1 gm. or more of the material determine loss on ignition (*i. e.*, water of hydration) Portland showed 10.19 to 13.10 per cent (average 11.46), slag cement gave 0.70 to 0.84 (average 0.78) per cent.

The amount soluble in water also differs. Shaking 1 to 1.5 gms. with 3 liters of freshly boiled water, and collecting and weighing the residue after ignition, indicated that there was dissolved out from Portland cement (28.7 to 42.8) an average of 37.15 per cent., but from slag cement 1.2 to 4.56 (average 2.33) per cent.

Potable Waters—Iron and Phosphates. Causse (*Bull. Soc. Chim.*, XXX., 1229). The water is filtered, and to a volume of 2 or 3 liters is added 0.6 to 0.8 gm. per liter of cloromercurate of para-amidobenzene sulfonate of sodium. After vigorous agitation the salt partially dissolves leaving temporarily a clear solution, but very soon the reaction begins, and it begins to cloud. It must be allowed to stand until it has completely clarified by sedimentation, which requires 24 to 36 hours and sometimes more.

If the water is pure and contains little or no iron the precipitate is white and crystalline. If the reverse is the case, it is curdy and grayish while the supernatant water has a brownish tint. After settling the water is decanted, and the sediment with the water adhering transferred to a tube. On adding HCl this will dissolve clear if the water was pure. If not, an insoluble residue of Hg_2Cl_2 remains undissolved.

The Fe and phosphates have been dissolved by the HCl. This is filtered off, evaporated to dryness, and fused with Na_2CO_3. On extracting with water the phosphate is dissolved out, and may be estimated by means of molybdate, etc., while the Fe may be dissolved in acids or by fusion with $KHSO_2$ and also estimated.

Examination of Asphalts. Lunge and Krepelka (*Chem. Ztg.*, XXVIII., 178). The object of this investigation was to find, if possible, means of distinguishing between natural asphalt products made from petroleum pitch and those from coal tar pitch.

The specific gravities (determined in Sprengel tube) were found to be 1.1 or under for natural and petroleum asphalts, the natural asphalts being as a rule lower (though gilsonite showed 1.17). Coal tar pitch was usually 1.2 or over. Similar differences were shown by sp. gr. of 6 per cent. solutions of the asphalts in chloroform. In one extreme case a 6 per cent. solution of "petroleum asphalt" (in $CHCl_3$) had a gravity of 1.47, while the coal tar pitches show 1.475 and over. Dissolving any of these substances in $CHCl_3$ always shows a diminution of sp. gr., not an increase, so that the solution seems to have more the character of a mixture. Chloroform of sp. gr. 1.4915 when holding 6 per cent. Bermuda asphalt shows a sp. gr. of 1.4595, etc. The melting points gave no means of distinguishing.

The iodine figures for the different materials ranged from 23.37 to 46.99 (with one exception 54.10) for natural asphalts, for "petroleum asphalts" 44.26 to 52.02, and for coal tar pitches 64.39 to 69.34.

Petroleum benzin added to chloroform solution of coal tar pitch gives a precipitate which is not the case with the other two classes.

BOOK REVIEW.

The Proceedings of the Chemical and Metallurgical Society of South Africa, with appendix. February, 1897, to September, 1899, Volume II. Published by the Society at Johannesburg, Transvaal. New York, Engineering Mining Journal, 928 pages, cloth, 8vo.

The prominence that the Chemical and Metallurgical Society of South Africa has attained within the last few years, as shown by the frequent reprints of its papers in the technical journals devoted to mining and metallurgy, leads one to look with particular interest through the collection of papers which constitute Volome II. of the Proceedings of the Society.

Owing to the location of the Society within the borders of the World's greatest gold producing region, the proceedings are for the most part concerned with the metallurgy of gold and subjects closely related. The cyanide process in many of its phases, especially comes in for a large share of the pages. In fact the volume might almost be called a treatise on the cyanide process as carried on in South Africa, for it discusses South African practice in great detail.

Each paper, after its reading, is fully discussed by the members of the Society, the discussion in several cases waxing rather warm and certainly serving to increase the readers interest in the subject in hand.

Among the papers contained in the volume, not bearing directly on the metallurgy of gold, are those of Professor A. von Oettingen, occupying the chair of physics at the University of Leipzig, on the "Theory of Solutions," and "The Theory of Dissociation as Applied to Galvanic Currents," which are of great interest as pointing the way to the application of the most modern scientific thought to the theory of some phases of the cyanide process.

A number of the papers discuss assay practice in general and as carried on on the Rand. Among them are "The Assay of Mill Bullion," by T. W. Wood; "The Assay of Graphite Crucibles," by A. F. Cross and others; "Assaying Gold Bearing Materials," by W. Bettel; "The Position of the Assay Department in Mining Economics," "The Accuracy of the Fire Assay," "The Scorification Assay," and "The Liquation in Cyanide Bars," by other members.

The papers of the greatest interest and value in the volume are those on the treatment of slimes by the cyanide process. Such authorities as John R. Williams, Charles Butters, W. A. Caldecott and A. F. Crosse contribute papers and discussions. Among these papers are "The Indirect Advantages of a Slimes Plant," by J. R. Williams; "The Solution of Gold from Slimes," by the same author; "The Economic Treatment of Slimes," by Charles Butters; "A Continuous Process of Slimes Treatment," by E. T. Rand. The theory of the coagulation of slimes and their settling is fully and most interestingly discussed.

A number of papers discuss the question of precipitation of gold from cyanide solutions, among the authors being two from our own country, Professor S. B. Christy of the University of California, and Mr. George A. Packard of Massachusetts, Mr. T. Lane Carter contributes "The Precipitation of Gold by means of Zinc," Professor P. de Wilde of Brussels University, "The Precipitation of Cyanide Solutions by means of Copper Salts." Professor Christy, "The Solution and the Precipitation of Gold from Cyanide Solution," and Mr. G. A. Packard, "Zinc Dust Precipitation," Mr. A. von Gernet and others discuss fully Electrolytic Precipitation.

Papers of particular interest to the analytical chemist are the "Estimation of Oxygen in Cyanide Solutions," by A. F. Crosse, "Notes on the Estimation of Sulphides in Cyanides," by Dr. J. Loevy, and "The Estimation of Protective Alkali," by A. F. Crosse.

Mr. H. T. Durant contributes an important paper on the "Oxygenation of Cyanide Solutions," and Mr. E. H. Johnson contributes "The Relation of the Stamp Milling of Gold Ores and Cyaniding."

Other papers of interest are "Experimental Metallurgy," by T. E. Clennel, relating to laboratory experiments on ores, "Mine Surface Sampling," by S. H. Pearce, discussing the sampling of ore and mill products at the surface and in the mill, "The Losses of Gold in Mill Water," by A. von Gernet. There is also some very interesting discussion concerning cyanide poisoning.

At the end of the volume is an abstract of current literature concerned mainly with the metallurgy of gold and kindred subjects, which is very complete and serviceable. The book is one of great interest and value to those concerned with the metallurgy of gold.

CHARLES H. FULTON.

Woodbridge School,

FORMERLY

School of Mines Preparatory School.

---

417 Madison Avenue,

Between 48th and 49th Streets, NEW YORK CITY

Twenty-second Year Begins October 1st, 1904.

THE school is well equipped with physical and chemical laboratories, in which the students are required to perform a complete set of experiments illustrative of their recitations in physics and general chemistry. A special laboratory is devoted to qualitative chemical analysis for advanced students.

Five hundred Students of Columbia School of Mines have been instructed in the Woodbridge School. Also a large number have been prepared for Massachusetts Institute of Technology, Stevens Institute, Sheffield Scientific School, Lawrence Scientific School, Troy Polytechnic Institute, Cornell University, and the Classical, Medical and Law Departments of Harvard, Yale, Columbia and Princeton.

A summer school for students who have failed in June begins August 13th and coaches men for the Fall examinations. All classes are limited to five. College men are coached in Freshman and Sophomore Mathematics and Quantitative Analysis.

An advanced course for older students prepares them to enter the second year class. Last June one of our students received his degree in Electrical Engineering in three years.

VOL. XXV. No. 4. JULY, 1904.

THE SCHOOL OF MINES QUARTERLY.

A

JOURNAL OF APPLIED SCIENCE.

BOARD OF EDITORS.

A. J. MOSES, Prof. of Mineralogy.
J. F. KEMP, Prof. of Geology.
R. PEELE, Adj. Prof. of Mining.
R. E. MAYER, Adj. Prof. of Drawing.
E. WALLER, Analytical Chemist.
W. H. FREEDMAN, E E.,
T. H. HARRINGTON,
Tutor in Drawing

Managing Editor, R. E. MAYER,
Business Manager, T. H. HARRINGTON.

CONTENTS:

A Simple Dynamometer. By W. J. Spiro..... 343
A Crucible Charge for Gold and Silver in Zinc Ores. By E. J. Hall and E. Popper 355
Gathering Engineering Cost Data. By Halbert P. Gillette..... 358
The Detailed Design of a Railroad Bridge, Part II. By Wm. H. Burr, C.E. and Myron S. Falk, C.E..... 368
Notes on Metallography. By William Campbell.. 350
Abstracts — Notes on Recent Mineralogical Literature. By Alfred J. Moses and Lea McI. Luquer..... 412
Book Reviews..... 428

COLUMBIA UNIVERSITY

NEW YORK CITY.

Registered at the New York Post Office as Second Class Matter.

TWO DOLLARS PER YEAR. FIFTY CENTS PER NUMBER.

All Remittances should be made payable to Order of "The School of Mines Quarterly."

Portland Cement

THE LAWRENCE CEMENT CO.

ESTABLISHED 1832.

ERNEST R. ACKERMAN, President

This Company has manufactured and sold during 70 years upwards of **20,000,000** barrels of Cement; marketing the product in all the principal cities of the United States, Canada, West Indies, Philippines and South America.

The old Custom House on Wall Street, built in 1835–37, and the new Custom House on Bowling Green, now under construction, were built with cement sold by this Company.

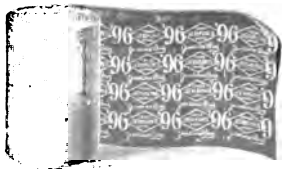
Used on the Old and on the New Stock Exchange in New York City, on the Brooklyn Bridge and New East River Bridge, and on the new Chamber of Commerce Building.

Detailed list of important Government Work. Reservoir Dams, Sidewalks, Fortifications, Bridges, Municipal Buildings and Railroad Work where "DRAGON" has been used, furnished on application.

DRAGON PORTLAND CEMENT Stands the Highest Requirements of Architects, Engineers and Builders.

SALES OFFICES:

NEW YORK, No. 1 Broadway. 15th and Market Sts., PHILA.



Time and Steam cost money.
Leaky steam joints waste them fast.

JENKINS '96 PACKING

which is absolutely guaranteed, saves both. Insist on having packing stamped with Trade Mark as shown in the cut if you would have the genuine.

JENKINS BROS.

NEW YORK, BOSTON, PHILADELPHIA, CHICAGO, LONDON

THE

SCHOOL OF MINES

QUARTERLY.

VOL. XXV. JULY, 1904. No. 4.

A SIMPLE DYNAMOMETER.*

BY W. J. SPIRO.

When a factory or manufacturing plant is located in a city, where ground rent is high, it is necessary that it cover the least practicable area, the necessary amount of floor-space being secured by building it two or more stories in height. This introduces the problem of transmitting the motive-power needed to drive the various machines and tools, from one floor to another, with the least possible loss and at the lowest possible expense.

There are at present recognized three solutions of this problem. The first, and that which has the sanction of long-continued practice and widest use, employs a series of line-shafts, one for each floor, driven by a system of belts running vertically or diagonally from floor to floor. The friction and other losses in such a system are large, being stated by various writers to be from twenty-five to forty per cent. of the power input, the exact percentage of loss depending upon the size of the building, number of floors, variety and condition of the transmission machinery, etc.

The second system is what is known as "electrical drive," and consists in first transforming the power into electrical energy by means of a dynamo, then transmitting it over copper wires to the various parts of the plant, and finally transforming it into mechanical work by means of electric motors attached to the machines to be

* This apparatus was constructed under the direction of Dr. C. E. Lucke, of the Mechanical Engineering Department of Columbia University, to be used for a test of a vertical shaft in a New York manufacturing concern.

driven, or to the line-shaft. The losses in a system of this nature are easily determined, since they consist of the sum of: (1) The loss in the generator or dynamo; (2) the copper or "C^2R" loss in the conductors; and (3) the loss in the motors, and in belts and shafting if they are used. It has been demonstrated that for plants of considerable size the electrical drive consumes less power than the system of belt and shaft transmission, and this, together with its many other advantages, is leading to its introduction and use in many modern establishments.

The third method of power-transmission consists of a vertical shaft extending from basement to roof, which is driven by belt

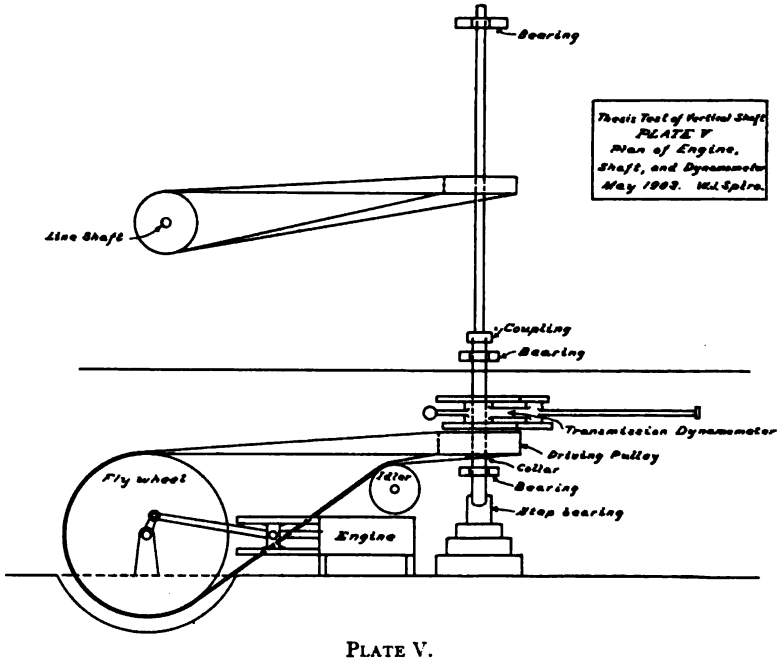


PLATE V.

from the engine, and from which quarter-turn belts at each floor drive the several line-shafts. This system, though but little known and used, nevertheless possesses many advantages, from the points of view of economy, safety and convenience, and an investigation of its merits, with special reference to the determination of the energy necessary to drive the vertical shaft under all conditions of load, should lead to useful results. It is the object of this paper to present the results of such a test, made on a shaft used in the works

of the Columbia Typewriter Manufacturing Company, of 116th street, New York City, and transmitting fifty horse-power to the six stories of the building. A sketch of the plant, showing the relative positions of the engine, vertical shaft, line-shafts, belts, etc., will be found appended hereto (Plate 5).

In order to perform this test a special transmission dynamometer was designed and constructed, and was used to measure: (1) The power to drive the vertical shaft alone; (2) the power used up in the quarter-turn belts; and (3) the power necessary to drive the entire transmission system of vertical shaft, line-shafts and belts.

Before entering upon the discussion of the test itself, it will be well to consider in detail the dynamometer referred to above, as upon this depends the accuracy and reliability of all the results obtained. The instrument bears some resemblance in principle to the Webber differential dynamometer, described at page 227 of Carpenter's "Experimental Engineering," but is designed to overcome the various drawbacks of the latter, chief among which is the fact that the driving and the driven shafts must revolve in opposite directions.

The main point in view in designing the instrument used in this test has been to produce an apparatus which would do the work required of it without in any way interfering with the operation of the plant to be tested, and without requiring any extensive alterations to the latter. Thus, it was necessary that both the engine and the vertical shaft should revolve in their usual directions, since (*A*) the engine was not susceptible of reversal; and (*B*) if the motion of the shaft were reversed the quarter-turn belts would run off. Further, no change in the shaft itself or in any of the pulleys or belts would be permitted by the owners. The instrument must be complete in itself, and require no modification of the plant to be tested, other than the loosening of the driving-pulley on the vertical shaft. Let us see how these conditions were met in the instrument as designed.

Referring to Plate 1 below, *S* is the vertical shaft, normally driven by a pulley (not shown) over which passes a quarter-turn belt from the engine fly-wheel. For the purpose of the test this pulley was loosened on the shaft and connected by straps to gear *B*, which also revolves loosely on the shaft, and which will hereafter be called the driving gear. *E* is an arm revolving loosely on shaft *S*, and carrying at its other extremity the arbor *M* to which are

keyed the pinions *C* and *D*. The gear *A* which meshes with the pinion *C* and will be called the driven gear, is clamped rigidly to the vertical shaft *S*. Into the extremity of the arm *E* is screwed a length of gas-pipe *F*, carrying a ring *G*, to which is attached one end of a spring-balance *T*, the other end of which is rigidly attached to a beam. The other end of the arm *E* carries a shorter length of pipe, on which slides the leaden ball *H*. This ball may

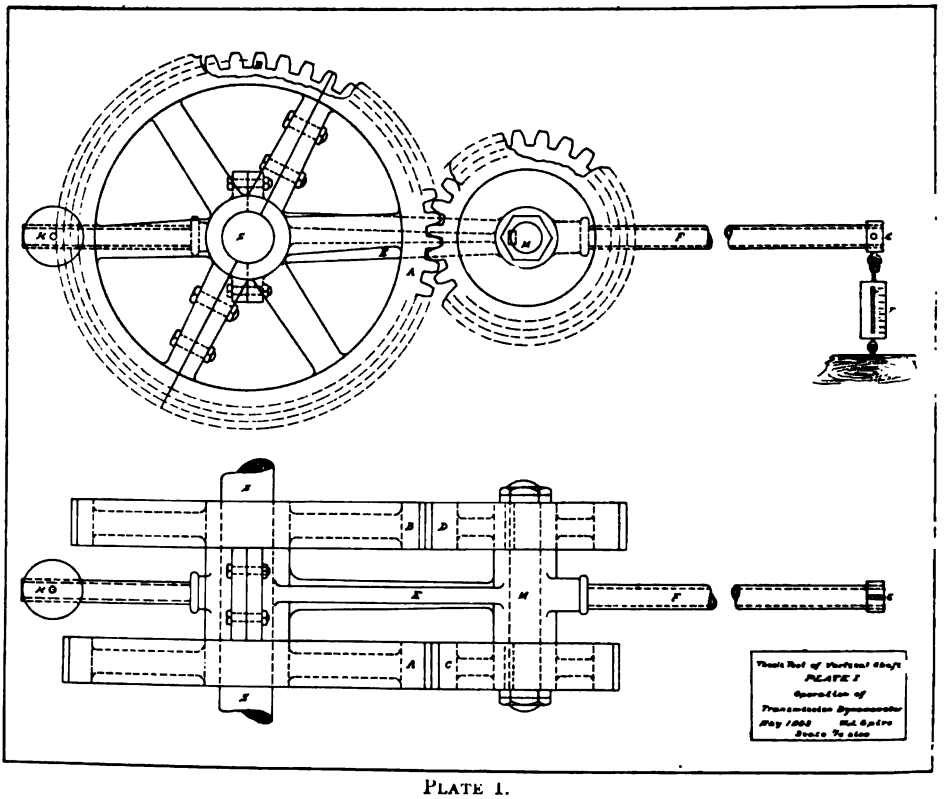


PLATE 1.

be fastened by a set-screw at any point of the pipe on which it slides, and its purpose is to counterbalance the weight of the arm *E*, the pinions *C* and *D*, and the pipe *F*.

The operation of the dynamometer is as follows: The power of the engine is transmitted by the quarter-turn belt to the driving-pulley, and thence to the driving-gear *B*. This gear meshes with and drives the pinion *D*, which in turn drives the pinion *C* through the arbor *M*, to which both are keyed. The pinion *C* drives the

gear A, which is rigidly connected to the shaft S, from which the power is taken off by quarter-turn belts at the various floors.

Now, as long as the arm E remains stationary, the engine will drive the vertical shaft positively, through the train of gears. But let us suppose that so great a load is applied to the shaft S as to hold it, together with the gear A, immovable, and let us further suppose that the arm E is free to revolve about the shaft S. Then, owing to the differential action resulting from the difference in size of the gears A and B and the pinions C and D, the entire power of the engine will be consumed in rotating the arm E about its shaft. To prove this, let us suppose that gear B has 90, D 60, C 50, and A 100 teeth. Then, when gear B makes one revolution it will have revolved pinion D through $90/60 = 1\frac{1}{2}$ revolutions. Pinion C will, of course, have made $1\frac{1}{2}$ turns also, which in its case is equivalent to $1\frac{1}{2} \times 50 = 75$ teeth; and since gear A is stationary, this will have caused the arm E and its pinions to rotate about S through 75 teeth of A, which is equal to $\frac{75}{100}$ or $\frac{3}{4}$ of a revolution. Thus, for every revolution of the driving-gear the arm E will revolve $\frac{3}{4}$ of a turn about S.

Now, if we assume the normal working conditions, *i. e.*, S carrying its normal load, and motion of E resisted by the action of the spring-balance T, then it will be evident that the power applied at B may be expended in either of two ways: it may rotate the shaft S, thus carrying the machinery-load, or it may revolve the arm E about that shaft against the resistance of the spring-balance T. Since any force always chooses the path of least resistance, the engine will choose that one of the two alternatives which demands the expenditure of the least amount of power. What will actually happen is this: The rotation of the gear B will cause the arm E to revolve until the resistance of the spring-balance is just equal to the resistance to motion of the shaft S. Further revolution of B will then cause revolution of S, T remaining in a position corresponding to the load on S. The balance T will therefore measure the pull necessary to revolve the shaft S, and since we know the effective length of the arm E and the number of revolutions of B per minute, we may calculate the horse-power input necessary to revolve the shaft together with its load.

Such is the principle of the transmission dynamometer, and it will be seen that its use necessitates no alterations in the plant, other than the loosening of the driving-pulley on the shaft S.

Furthermore, this driving-pulley will revolve in the same direction, and at nearly the same speed, as the shaft, and will therefore be free from any tendency to heating.

It now becomes necessary to consider the practical design and construction of the dynamometer to meet the conditions of its use.

The gear-teeth were calculated by means of the formula $W = spfy$ (Kent, p. 901), and it was found that to transmit 50 horse-power at 200 R.P.M., gears of 2 diametrical pitch and 3-inch face would be required. The arms of the gears and the webs of the

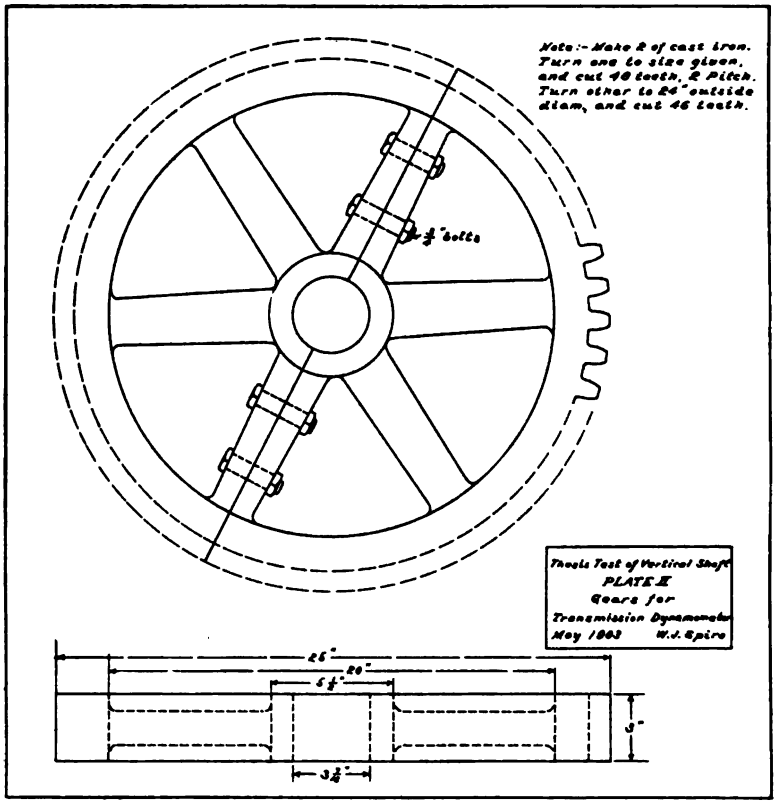


PLATE II.

pinions were calculated as cantilevers fixed at the hub and loaded at the circumference, but they, as well as most other parts, were made considerably larger than called for by the calculations, in order to give the necessary stiffness.

The arm *E* was designed for stiffness, since the stresses to which it is subjected are not great. Standard sizes of bolts and pipe were used where required.

It being impossible to obtain stock gears to fill the requirements, and in order to economize time and labor as much as possible, it was decided to make but one pinion-pattern, proportioned for the larger pinion, and to make two castings from this, turning one of them down to the size of the smaller pinion. Similarly, a pattern for one half of the larger gear only was constructed, four castings

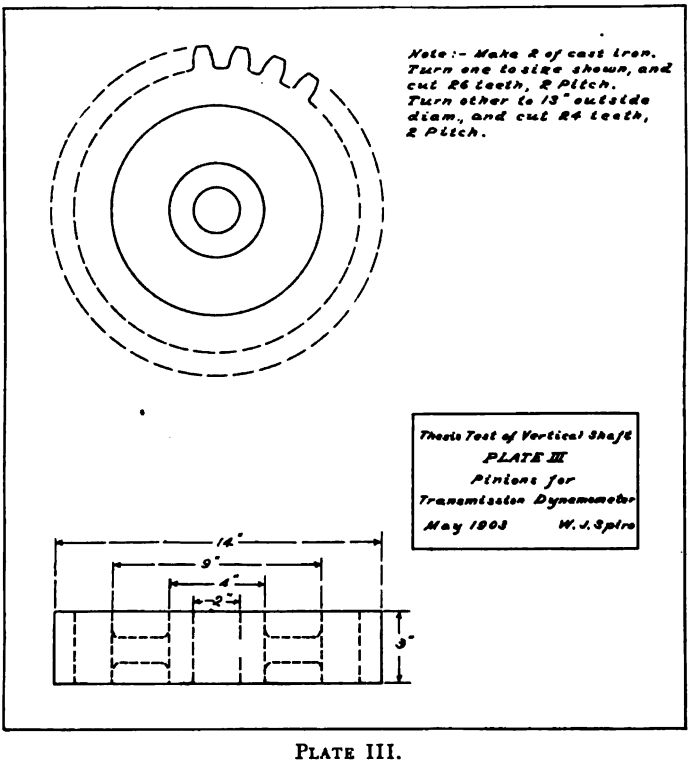

Note:- Make 2 of cast iron. Turn one to size shown, and cut 26 teeth, 2 Pitch. Turn other to 13" outside diam., and cut 24 teeth, 2 Pitch.
Thesis Test of Vertical Shaft
PLATE III
Pinions for
Transmission Dynamometer
May 1903 W. J. Spire
14"
9"
4"
2"
3"

PLATE III.

being made from this, and bolted together in pairs to form the two gears, of which one was turned down to the size of the smaller or driving-gear. This necessitated making the rims of the larger gear and pinion somewhat heavier than called for by the calculations, but it is believed that this was justified by the saving in pattern-work. Plates 2, 3 and 4 are scale-drawings of the pinions, gears and arm, and from these the several parts were made, oil-grooves and oil-holes being provided where these were needed.

It will be seen from the drawings that the numbers of teeth in the gears and pinions are as follows: Gear A, 48 teeth; gear B, 46 teeth; pinion C, 24 teeth; and pinion D, 26 teeth. Now if A be held rigid, and arm E be revolved about shaft S, then when it has made one complete revolution the pinion C will have made $48/24 = 2$ revolutions, as will also the pinion D. As this latter pinion has 26 teeth, it will, during a revolution of the arm E, move over 52 teeth of B. But since B has only 46 teeth, it will have to move $52 - 46 = 6$ teeth in the direction opposite to that of E's

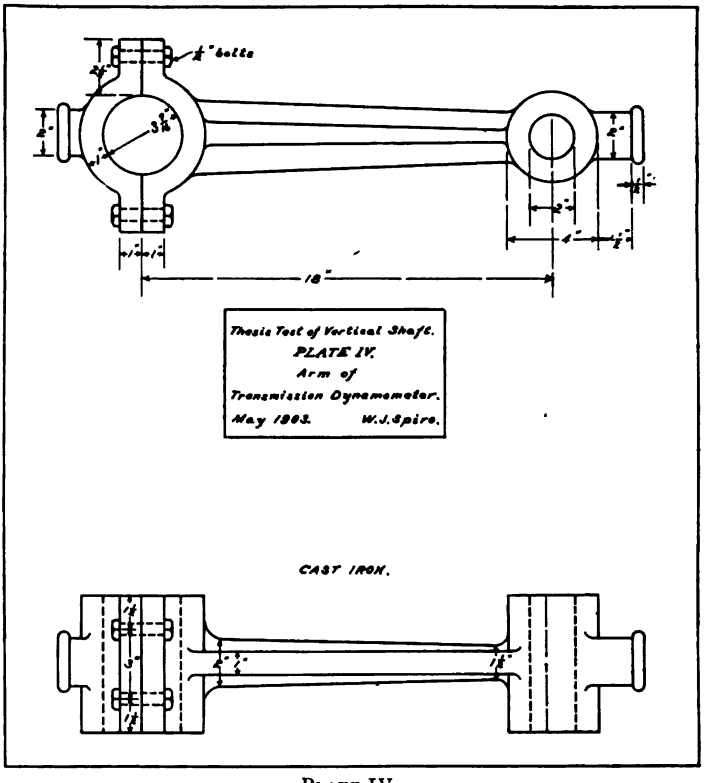


PLATE IV.

rotation in order that the above conditions may hold. Thus, whenever B gains 6 teeth, or $\frac{6}{46}$ of a revolution on A, the arm E will make one complete revolution about S. From this it follows that E revolves with but $\frac{6}{46}$ of the force, or pull, which tends to cause revolution of B. Thus, if we measure the pull at the balance T, and multiply this by the effective length of the arm E–F,

we must multiply this product by $\frac{48}{6}$ or $7\frac{2}{3}$ in order to get the moment of the gear *B*. Multiplying this by the number of revolutions per minute made by *B*, and by 2π, and dividing by 33,000, we shall have the horse-power input for any load. This may be otherwise stated as follows: $HP = 2\pi PLNC/33{,}000 = PN2\pi LC/33{,}000$, where $C = 7\frac{2}{3}$.

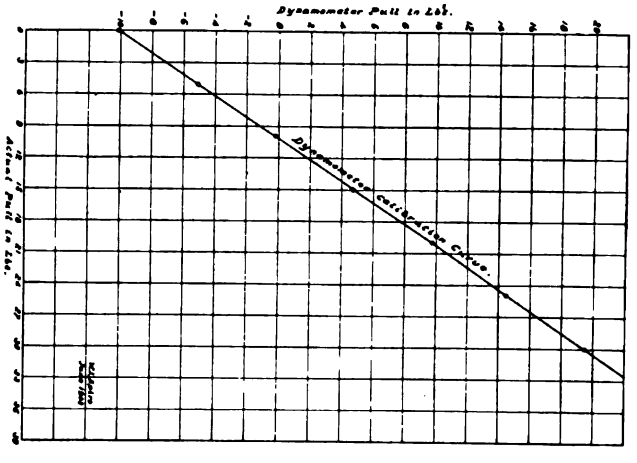
For any given length of arm *L*, the product $2\pi LC/33{,}000$ is constant, and in order to find the horse-power input we need only multiply the product of the balance-reading and the R.P.M. by this constant. The process will be still further facilitated if the constant be some even fraction, such as .01. Let us see what length of the arm *E* would make the constant take this value. We will have $2\pi LC/33{,}000 = .01$, whence, solving for *L*, we have $L =$ 6.8506 feet, or 6 feet 10.2 inches. Thus if we fix the ring *G* (Plate 1) at 6 feet 10 inches from the center of the shaft *S*, then to find the horse-power input at any load we need only multiply the balance-reading by the R.P.M. and point off two places. Similarly if we make $L = 3$ feet 5.1 inches, then the constant will be $\frac{1}{200}$, and if $L = 2$ feet 3.36 inches the constant is $\frac{1}{300}$. Marks representing these lengths of lever-arm are accordingly made on the pipe *F*, and the ring *G* may be brought to any of these marks, and there fastened by means of a set-screw.

The various parts of the dynamometer having been completed and assembled, the instrument was placed in position on the vertical shaft, the weight of its parts being supported by a collar fixed on the shaft. Arms (not shown in the drawing) extended upward from the gear *B*, engaging with the spokes of the driving-pulley, while similar arms extending from gear *A* engaged with the spokes of another pulley, loose on the shaft, to which the band of the prony brake was applied.

The spring-balances of the dynamometer and the prony brake having been calibrated by means of weights, and being found sensibly correct, the calibration of the dynamometer itself was next undertaken. For this purpose gear *A* was not clamped to the vertical shaft, but was allowed to revolve loosely thereon, liners being put between its two halves to accomplish this. The band of the prony brake being loose, the engine was then started, whereupon the arm of the dynamometer swung around in the opposite direction to that in which it was expected to turn. It was soon seen that, there being no load on the gear *A*, the friction of the

various parts was carrying the entire arm around in the same direction as that in which the driving-pulley revolved. The spring-balance being removed to the other side of the arm, and the engine being again started and brought up to speed, it was seen that the friction produced a practically constant pull of 10.1 pounds on the balance at a radius of 2 feet 3.36 inches, corresponding to pulls of 6.72 pounds and 3.36 pounds at radii of 3 feet 5.1 inches and 6 feet 10.2 inches respectively. If we regard pulls in this direction as negative, then it is evident that we must subtract from the scale-readings at any load the constant friction-pull above determined, in order to obtain the actual pull due to the load.

Proceeding thus, the prony brake was now put into service, and simultaneous readings taken of the brake and dynamometer scales



(Table I.). From a comparison of these readings it was found that the friction-loss in the dynamometer increased slightly with increase of load. After a load of about 20 horse-power was reached it was found impossible to proceed with the prony-brake, owing to the lack of provision for cooling the latter.

During this test, and while the engine was running at full speed, part of the mechanism became deranged, causing the dynamometer arm to come in contact with the rim of the driving-pulley, the rapid revolution of which created a shower of sparks and tended by friction to pull the arm around with it against the resistance of the spring-balance. The engine was stopped as quickly as possible, and just as it ceased turning, the pipe forming the weighing-arm

of the dynamometer broke off at the thread under the excessive strain, leaving the rest of the apparatus free to revolve with the driving-pulley. If this had occurred while the engine was still in motion, the arm in its revolution would have brought up against a brick wall, and would undoubtedly have sprung the vertical shaft and seriously damaged the instrument.

The dynamometer having been calibrated, a test of the power consumed by the vertical shaft at various loads was next in order. For this purpose the gear *A* was clamped tight to the vertical shaft, as was also the pulley on which worked the prony brake. Load was now applied to the latter, and was transmitted through the vertical shaft to the dynamometer, where it was measured. The readings and results, as tabulated below (Table II.), show that the loss in the shaft is nearly constant at all loads, and amounts to only about 1 ¼ horse-power.

The next and last part of the test consisted in ascertaining the power required to drive the belts and shafting forming the power-transmission system of the factory. The prony brake was removed, and the quarter-turn belts at the various floors were put on one by one, the load due to each belt and line-shaft being measured at the dynamometer. Table III., which gives the result of this test, shows that the power required to drive the transmissive machinery constitutes only about 20 per cent. of the total power consumption, proving that the vertical-shaft transmission involves a saving in power of from 5 to 20 per cent. over the common belt-transmission.

It was desired that all tests be made at the normal speed of revolution of the shaft, and since the interposition of the dynamometer reduces the shaft to $\frac{23}{26}$ of the speed of the driving-pulley, it was necessary to speed up the engine so as to make the driving-pulley revolve 204 times per minute in order that the vertical shaft might make its normal 180 R.P.M. The speed during the entire test was kept constant by the engine-governor, though this was checked at frequent intervals by the use of revolution-counters.

It was found that, especially at high loads, the fluctuation of the dynamometer-scale was considerable, though this could be greatly reduced by a proper adjustment of the balancing-arm *H* (Plate 1). In future use of the instrument it might be well to attach a dash-pot in order to overcome this fluctuation. It would also be desirable to replace the 1-inch pipe *F* (Plate 1) by a solid rod, which would obviate the possibility of breaking at the thread.

The dynamometer is, of course, bored out to operate on a $3\frac{7}{16}$-inch shaft, but if a set of bushings be made for the gears and arm it might be used equally well on smaller shafts. If gear A be made the driver, instead of gear B, then the arm F will always revolve in the same direction, which will make it unnecessary to reverse the position of the spring-balance during the test.

TABLE I.

CALIBRATION OF DYNAMOMETER.

A	*B*	*C*
—10.1	0	0
— 5.1	15	5
— .2	30	10
4.75	45	15
9.75	60	20
14.5	75	25
19.55	90	30

NOTE.—Column A contains the readings of the dynamometer scale, the length of its arm being 2 feet 3.36 inches.

Column B contains the readings of the prony brake scale at an arm-length of 5 feet 10 inches.

Column C contains the calculated values of these readings for an arm-length of 17 feet 5.9 inches, which would correspond to the actual length of the dynamometer arm, taking into account the differences in leverages.

These readings will be found on the curve, p. 352, from which the actual value of the load-pull corresponding to any value of the dynamometer reading may be readily determined.

TABLE II.

TEST OF POWER REQUIRED TO DRIVE VERTICAL SHAFT AT VARIOUS LOADS.

A Prony-Brake Pull.	*B* Load in H. P.	*C* Dynamometer Pull.	*D* Corresponding Pull at no Load	*E* Dynamometer Pull due to Load	*F* H. P. Required to Turn Shaft.
0	0	—8.3	—10.1	1.8	1.224
15	3.4	—3.25	— 5.1	1.85	1.258
30	6.8	1.6	— .2	1.8	1.224
45	10.2	6.55	4.75	1.8	1.224
60	13.6	11.6	9.75	1.85	1.258
75	17	16.4	14.5	1.9	1.292
90	20.4	21.4	19.55	1.85	1.258

NOTE.—Speed of driving gear = 204 R.P.M. Length of prony brake arc = 5 feet 10 inches. Length of dynamometer arm = 2 feet 3.36 inches. Column B is computed from Column A by the formula H. P. $= \frac{2\pi PLN}{33000} = \frac{PN}{900} = \frac{17P}{75}$. Column D is taken from the calibration test of the dynamometer. Column E is the difference between the readings of Columns C and D. Column F is obtained by means of the formula: H. P. $= \frac{2\pi PLN}{33000} = \frac{17P}{25}$.

This transmission dynamometer should prove useful in making tests on various types of machine-tools to determine accurately their power-consumption as well as to find the losses in transmission systems, the relative efficiencies of rope and belt drives, etc. The fact that it can be operated on a line-shaft without change or injury to the latter should make it useful for making tests in factories up to the limit of its capacity (about 100 H. P.). In fact, it is hoped that this test of a vertical shaft will prove but the introduction to a wider field of endeavor in which the transmission dynamometer herein described shall play an important and useful part.

TABLE III.

TEST OF POWER REQUIRED TO DRIVE VARIOUS PARTS OF TRANSMISSIVE MACHINERY.

Run No.	*A* Increment of Load.	*B* Dynamometer Pull.	*C* Corrected Pull	*D* Increase of Pull.	*E* H P. Input.
1	Vertical Shaft.	—8.3	1.8	1.8	1.224
2	Base't Belts and Shaft.	—6.9	3.2	1.4	.952
3	1 Floor " " "	—5.8	4.3	1.1	.748
4	2 " " " "	—3.1	7.05	2.75	1.87
5	3 " " " "	—1.4	8.76	1.71	1.163
6	4 " " " "	1.1	11.31	2.55	1.734
7	5 " " " "	2.1	12.33	1.02	.694
8	Entire Shaft Load.	2.1	12.33	—	8.384
9	Full Working Load.	17.4	20.76	—	42.35

NOTE.—Speed of driving gear = 204 R. P. M. Length of dynamometer arm in runs Nos. 1 to 8 inclusive = 2 feet 3.36 inches; in run No. 9, 6 feet 10.2 inches. Column *C* is obtained from the curve of calibration of the dynamometer, by interpolating the values in column *B*. Column *E* is obtained from the formula: H. P. = $PN/300 = .68\ P$ for runs Nos. 1 to 8; and H. P. = $PN/100 = 2.04\ P$ for run No. 9.

It will be seen that run No. 8, or the total shafting and belt load, is 19.9 per cent. of column 9, which is the Full Working-load.

(Contributions from the Havemeyer Laboratories, Columbia University, No. 99.)

A CRUCIBLE CHARGE FOR GOLD AND SILVER IN ZINC ORES.

BY E. J. HALL AND E. POPPER.

Experiments have been conducted for the past four years by various members of the Chemistry Department aiming to improve or supplant the present scorification method of assaying zinc ores for the precious metals.

Investigations were made on the scorification assay using oxide of iron,* a combination method similar to that used for copper mattes, and a scorification charge using soda.

However, all of these methods proved to be just as troublesome as the ordinary scorification method, which frequently necessitates the use of but small amounts of ore (.1 A. T.), as well as constant attention and manipulation to prevent the formation of zinc crusts. Furthermore the results were no better.

Therefore the following investigations were conducted with the hope of eliminating both the troubles inherent in any scorification as well as the special difficulties met with in the scorification of zinc ores; by the use of a crucible method.

The preliminary work consisted largely in experimenting with nails and with nitri as desulphurizing agents on sphalerite, the most common zinc ore, and in studying the effect of varying the amounts of litharge, soda and borax glass.

Omitting the details of this work it is sufficient to say that, after making some two hundred fusions, the results indicated that the most satisfactory charge must contain:

(1) Only sufficient litharge to give a lead button of proper size to collect the gold and silver, on account of the difficulty in regulating the size of the button, and because lead oxide in the slag seems to interfere with the complete decomposition of the ore, and prevent the formation of a slag which is free from lumps and readily poured. (2) Soda (Na_2CO_3) four or five times as much as ore. (3) Borax glass sufficient to prevent the charge from being entirely basic and assist in fluxing the gangue minerals not acted upon by soda alone. (4) Argol, if necessary, sufficient to reduce all the lead.

It may be necessary to add a couple of nails if the ore is high in pyrite (over 15 per cent.) to prevent the formation of a brittle button.

The final charge adopted was:

Ore	½	A. T.
Soda (Na_2CO_3)	1½	"
Borax Glass	½	"
Litharge	⅔	"
Argol	O to X	

* Furman, "Manual of Practical Assaying" 5th ed., p. 124.

The reason for using only one third A. T. of ore is the tendency of the charge to boil excessively, and the danger of overflowing when a larger charge is run in a 20-gm. crucible. This boiling is not caused mainly by decomposition of the ore, but apparently by the action of soda on the silica of the crucible, as it may continue long after fusion is complete. The charge given is very similar to that of Arron.

The experiment was made of varying the temperature (measured with a Le Chatelier pyrometer) and it was found that best results were obtained from 750–775° C. Above this temperature (which is about that of scorification) the results were lower, in some cases considerably below the scorification figures. The time required in the muffle was from thirty to thirty-five minutes.

In view of the fact that an ore containing 15 per cent. of copper could not be satisfactorily run with this charge, experiments were made to determine the amount of copper which could be taken care of. Ores were made containing varying percentages of copper sulphide, and it was found that ores containing up to seven and one half per cent. of copper could be satisfactorily assayed.

There is no doubt in the minds of the investigators that the charge could be used for one half A. T. of ore, the fluxes being increased proportionately, if the fusions were made in a thirty gm., low form, crucible (Denver Fire Clay Co.).

The results compared with scorification follow:

Ore.	Per cent. Zn.	Scorification .1 A. T. Oz. Au and Ag per Ton.	Crucible 1/3 A. T. Oz. Au and Ag per Ton.
1	2.5	48.00	48.20
2	5	10.00	10.41
3	6	9.70	9.78
4	8	42.50	42.54
5	9.5	165.00	168.48
6	11.5	125.80	129.40
7	11.5	38.00	37.95
8	17.5	17.10	17.16
9	27.5	135.80	139.35
10	29.7	85.00	87.66
11	35.6	105.70	106.56
12	44.0	71.10	73.83
13	47.6	44.80	47.28
14	52.0	40.10	41.34

The gold and silver beads were not parted as the gold present would not affect the comparison.

A study of the table will show that in every case the results by this crucible charge either checked or exceeded those obtained by scorification.

ASSAY LABORATORY,
COLUMBIA UNIVERSITY,
June, 1904.

GATHERING ENGINEERING COST DATA.*

BY HALBERT P. GILLETTE.

I purpose offering a few suggestions on the methods of securing and using cost data. I need not dwell long upon the use of such data; the difficulty consists in the finding of the data rather than in the application of them when found.

The dearth of information bearing upon the actual cost of doing work will soon become apparent to many of you, if my own early experience in any degree typifies that of the average engineering graduate. I recall with distinctness the day when a farmer entered my office and asked for "the surveyor." Being informed that I was "the surveyor," his next question was, "What will you charge to subdivide a section of land for me?" I put the question to you, gentlemen — What would you charge to subdivide a section of land? You are doubtless quite as capable of answering now as I was then. After some "sparring," in which I asked the location of the land, the density of brush, and the like, I made a guess, naming $20 as the fee for the work. I remembered afterward that my farmer friend closed the bargain with alacrity. I, with my party (of one man), spent just six days chopping brush, not to mention two days finding lost corners, so that when the center of the section had been located, I turned over the $20 to my party for wages, and, as for myself, I had left the cost data. Few of you are likely to have just such an experience, but many of you will have experiences not so greatly dissimilar.

The lawyer and the doctor are not expected to submit their bills until their work is done. The engineer, however, because he is a master of exact science, is presumed to be gifted with exact foresight even as to bills for his own services. So you need not be surprised if some prospective client, who contemplates

* Abstracted from a lecture delivered before the civil and mining engineering students of Columbia University, November 24, 1903.

building a trolley line, asks you what the survey will cost, and takes out his note-book to record the reply before you can catch your breath.

Fortunately, there is a good deal in print relative to the cost of different kinds of surveying, but unfortunately, and strangely enough, these surveying cost data are not ordinarily to be found where you would most expect to find them, namely, in text-books on surveying. In view of this condition of affairs, I advise you to record in a note-book every bit of information that you can secure relative to the cost of surveying; and I would go farther in advising you to record the time that you yourselves take to do the various pieces of field work at the summer schools of surveying. This you should do not so much for the few cost data that you will obtain while making these practice surveys, but for the habit that you will thus form — the habit of observing and recording the time consumed in doing work. Let me pause here to say that for the formation of a habit that has been invaluable to me, I am indebted to Professor Munroe; for, as a part of our summer school of mining work, we were required to record in note-books not only the methods of drilling, and the like, but the progress made — the cost of doing the work. The data that I thus gathered were not without value, but the habit that I thus formed has been to me invaluable.

Shortly after my first experience in the art of cost guessing I was called upon to locate a number of wagon roads through a new country, hilly and covered with dense forest. Having finished the survey and computation of quantities for a gravel and plank road some eight miles long, I submitted my plans and estimate of quantities. I was requested to submit also an estimate of the cost of each item of work. "What will it cost?" — the same old question again! Going to my office, I turned instinctively to the book that I had always supposed contained all that was known about the cost of engineering work. The first item that I had to consider was earth excavation, and I felt that on this item I should not be disappointed in putting my trust in the book. I found that, for the short haul in the roadwork under consideration, drag scrapers would be most economic; and, if my memory serves me right, I learned that about five cents per cubic yard would cover the cost of my road excavation. But when I stopped to consider it, that seemed a very low unit cost, and I recalled vaguely having seen

contract prices for road work that were much higher. However, I reasoned that the conditions governing my work probably differed from those governing other work, and surely I could not err very badly in accepting the data furnished by my book. Fortunately, my mind was not wholly at ease in spite of the book's elaborate tables of earthwork cost, and I finally resolved to find some local contractor and put the question to him as to what he would consider a fair price for earth excavation under the given conditions. I found my man, a Mr. Murphy I believe his name was. Mr. Murphy, after hearing my question, did not turn to his book, as I half hoped, half expected he would, but without hesitation gave some twenty odd cents per yard as being a fair price for the work. In spite of the fact that he seemed very sure about it, I ventured to remark that Murphy and my book did not agree very closely. I was told in a few forceful terms that tables of earthwork-cost had been "the ruination of" more contractors than Mr. Murphy had fingers and toes. I was informed that a book was "very good for the theory," but worse than useless for "the practice."

I may say here that, for fear of betraying your ignorance of costs, you need never hesitate to go to a contractor for information. I find that contractors, as a class, think that engineers, as a class, know next to nothing about the actual cost of work, and I fear that there has been altogether too much reason back of this belief. An older man is always flattered by having a younger man come to him for advice or for information, and contractors are no exception to this rule.

There is, however, another side to the reliability of this source of information. Contractors often err exceedingly in their estimates; and an experienced contractor is more likely to err than an experienced engineer where the work is new to both, the reason being that the engineer, by virtue of his mathematical training, is more likely to "figure out" every item rather than to "lump off" the unknown in one bold guess.

Reverting to my estimate, or perhaps I should more truly say to Mr. Murphy's estimate, of the roadwork, I was taught by it a very useful lesson, and incidentally the habit of keeping records of the cost of work coming under my observation was strengthened by this experience. I have since found that records gathered thus at someone else's expense are not the least valuable of an engineer's stock in trade.

There will come a time when some of you will be "out of a job," (at least that has been one of the experiences of a few of us who are older in the profession), but even then you may usually spend your time to good advantage if you are near the site of construction work. Let us assume for example that Fifth Avenue is being paved with asphalt, and that you have a little time at your disposal each day. In the morning you visit the work, count the men engaged, and observe their respective duties, all of which you enter on a scrap of paper to be afterwards copied into your permanent note-book. You talk with the foreman and learn from him what the average progress of the work has been, but under no circumstances do you rely entirely upon what he tells you. You note that the pavement has reached a point opposite No. 531, at a given hour, and then you go away to study some other work in the same way. Later in the day, or the day following, you return and pace the distance progressed since your previous visit when the end of the pavement was opposite No. 531. Thus you find out whether or not the foreman was somewhat of a liar, as occasionally happens. But the foremen are not necessarily liars even when they deceive you, for it often happens that they themselves do not know the average rate of progress. Foremen on pavement work usually do know what a fair day's work is, but on work less easily measured, they frequently do not. You may now watch the gang laying the concrete payment base for an hour, counting the batches and estimating the yardage; and upon comparing this short time observation with your record for the full day, you may learn something else — something about human nature. Should the output of the laborers for the hour's work exceed the rate for the full day by 50 per cent., or even 100 per cent., do not regard the short time observations as valueless. Look about. The contractor himself may be standing near by. The presence of the man who pays the men out of his own pocket often has a magic effect. Where laborers were averaging 12 cubic yards per day loaded with shovels, and where they were apparently working well, I have seen the output jump to 18 cubic yards and maintained day in and day out at that rate, simply because of a change in management.

Let me digress here to say a word about foremen. When a foreman comes to you seeking a position and mentions as one of his qualifications the fact that he is always popular with laborers,

and that as a consequence they will do more work for him than for other men — don't take any stock in that foreman. Men, as they are now constituted, do not work for the pleasure of pleasing a foreman. The "jollier" is good enough in his place, but his place is not as foreman of a gang of laborers. The same severity of discipline should be maintained as in the army. The foremen, who are in reality the officers, should keep aloof from the laborers socially, and should hold the men strictly to their tasks with little or no show of leniency. If you will choose extremes, choose the swearing foreman in preference to the "jollying" foreman. Advice of this kind sounds harsh, and so it is, but work is a harsh task for most of us in this world, and it takes harsh measures, often harsh language, to hold us to our duty.

I shall speak next of an experience in estimating the cost of bridge building. I designed two highway bridges of a modified Howe truss type, and, forming a partnership with an experienced bridge foreman, went about securing a contract. Of course it was not difficult to estimate the cost of the timber and steel delivered at the sites, but, when my partner and I put our heads together in an endeavor to agree upon an estimate of the probable cost of the labor of framing and erecting the bridges, our heads did not bump. Indeed we were about "100 per cent. apart," as someone put it. My partner guessed that $500 would cover the labor item on one bridge — a bridge with a 16-foot roadway, 160 foot span, designed to carry 100 pounds per square foot. I had all the books on bridge design and construction, but diligent search had failed to disclose a single scrap of information that would guide me in estimating the cost of building a Howe truss bridge, or in fact a wooden bridge of any sort. I turned to the files of the only engineering journal available, and finally I found just one little half-column article giving some costs for a Howe truss railway bridge reinforced with the wooden arches that were common in the early days of bridge building in this country. From the data there given, I estimated the labor on one of my bridges at $1,000 or 100 per cent. more than my partner's guess. We "split the difference" (a process not infrequently used by engineers and contractors) and we bid accordingly. The first bridge erected by us cost almost exactly $500 for labor plus $500 for materials. I think this is as good a record for economic bridge construction as is likely to be found. I feel safe in making the assertion, for,

although that bridge was built eight years ago, I have yet to find any published record of the cost of Howe truss bridge building other than the one that I mentioned a few moments ago. I shall not now give the itemized cost of this work, for my present purpose is not to give you data so much as to indicate how scarce data are and how desirable it is to form the habit of gathering and analyzing them.

Our next bridge went the way of many a good bridge over many a turbulent Western river. A freshet undermined the falsework, and let the bridge drop the day before its expected completion. When we had fished what was left of our bridge out of the water, when we had put it up again, and when we had settled the hospital bills (by a miracle there were no deaths) my original $1,000 estimate was exceeded. I learned by this accident two things: (1) Never to omit an allowance for accidents and other unforeseen contingencies; (2) never to neglect to insure the workmen. I shall digress to say a word about insuring laborers. Up to that time, I had supposed that if laborers were to be insured, it could of course be done by taking out a separate accident policy for each man — quite an expensive procedure as you doubtless know. After the accident I learned upon looking into the matter that a blanket policy covering all the men can be taken out, and that the premium is a given percentage of the pay roll; thus on earthwork you may insure all your men for less than one per cent. of the pay roll. This insurance does not give to each man a weekly stipend in case of accident, or to his heirs a designated sum in case of death. What the insurance company does do is to protect the contractor by assuming all liabilities from claims made by injured workmen or their heirs. The insurance company limits its liability, however, so that in case a number of men are killed by one accident, the contractor may have to stand part of the damages. No matter how safe the work seems to be, a contractor should never neglect to take out a pay roll insurance policy. Many a contractor, just starting in business, has been ruined through failure to insure against accident.

Taking up again the subject of cost gathering, I would impress upon you that you should not wait until you are in responsible charge of work before you begin gathering cost statistics. Many of you will find yourselves before long in the position of inspector on some engineering work of magnitude, and the very magnitude

of the work will probably discourage you in your determination to learn something about costs by your own observation. Let me assure you that you need not be in the least discouraged, that in fact you will probably be in a better position to acquire the most valuable kind of data than is the chief engineer himself. He, to be sure, will learn in a general way what each of the classes of work costs; but you, if you avail yourself of your opportunity, will learn in detail what certain parts of the work cost. I would sooner know every detail of the cost of a given kind of work on the New York Subway, for example, than to know in a general way what all the items cost, and let me explain to you why. Suppose that you determine to learn the cost of rock excavation where cableways are used to handle the excavated rock. You start by studying the cost of handling the rock with the cableway, and with your watch in hand, you note that at 9:15:10 (reading the hour, the minute and the second hand) the bucket begins to rise from the pit; at 9:15:20 it is out of the pit and begins its travel along the cable; at 9:15:40 it has reached the dump; at 9:15:55 it has dumped; and so on until it has made the round trip. Thus you time in detail a large number of round trips until you have a fair average for each element. You measure the lift and the distance of travel, and you note the kind and size of engine used; and when the plant is shifted from one place to the next you ascertain the lost time and the cost of shifting. What, you may ask, is the use of going so minutely into details? The answer is simply this, that you may be able to predict the cost of future work where some of the details differ, as for example the lift, or the length of the haul, or the number of times the plant must be shifted for a given yardage of excavation. Without such detailed data you will be unable to predict accurately but will have to guess. It is just this kind of detailed information that the chief engineer very likely will not get, so that, in fact, with all his seeming advantage he may not be able to predict the cost of similar work, where conditions vary somewhat, with as great accuracy as you can. Indeed I venture to say that on one job, thoroughly studied in detail, it is possible for a young engineer to learn more about actual costs than the majority of engineers learn in a lifetime.

Let me cite an example to emphasize the importance of a detailed knowledge of rock excavation. An engineer, a man of middle age who had seen a great deal of construction work, deter-

mined to bid upon one of the sections of the Erie Canal deepening work in 1896. He secured a contract at prices almost the same as those that had prevailed on the Chicago Main Drainage Canal, that is 75 cents a cubic yard for rock excavation and 28 cents for earth. To this engineer all canals evidently "looked alike." Canals, to him, were canals, and rock was rock; he gave no heed to the fact that on the Chicago Canal the rock was taken out in three benches, each twelve feet thick, whereas in the Erie Canal deepening one bench only two feet thick had to be removed. To this day I cannot account for that engineer's failure to make at least some allowance for the difference in conditions, but he did not, bidding for the rock about half the price received by other contractors. Of course, when he began to do the work and found how much of the time his cableways were idle during the frequent shifting necessitated by the shallow cut, when he found what an amount of drilling per cubic yard is necessary where the face is only two feet, and when he found that he had a great quantity of snow and water to handle for a few cubic yards of excavation, he learned that there is something besides words and names and bidding prices to be known by the contractor who would escape failure.

I am led by the foregoing example to add something concerning the use of bidding prices as a guide in estimating the cost of work. I think I may safely say that 90 per cent. of the engineers in practice base their estimates upon contractors' bids on a similar work. Where the rates of wages, the prices of materials and all the conditions governing the work are practically alike, this practice is a safe one; still I think that the practice is accountable for many of the failures of engineers who have attempted to go into the business of contracting. It is, on the whole, a practice not to be encouraged; but as we must all fall back upon it at times, I shall point out a few pitfalls to be avoided. Contractors very frequently unbalance their bids; by this is meant that they bid an unreasably high price on one or more items and offset it by bidding unreasonably low on one or more of the remaining items. To illustrate, suppose 20 cents per cubic yard is a fair price for earth excavation and that $1.50 is a fair price for rock excavation, then we might have a balanced bid like this:

10,000 cu. yds. earth at 20 cts. =	$2,000
200 " " rock at $1.50 =	300
Total	$2,300

Now suppose the contractor decides for one reason or another to unbalance his bid, and bids thus:

10,000 cu. yds. at 17 cts.	$1,700
200 cu. yds. at $3.	600
Total	$2,300

You will observe that his total bid is unchanged; yet in case it happens that far more than 200 cu. yds. of rock is encountered, he stands a chance of making a large and unjust profit by virtue of his lack of virtue, and because of his gift of foresight or shrewdness. There are many reasons for unbalancing bids, and some of them betoken no dishonesty at all; thus a contractor may wish not to disclose to his competitors what he regards as a fair price for a certain item, because he may intend bidding at any other time when that item will be the most important on the bidding sheet. I have known a few instances where dishonest contractors have unbalanced their bids, bidding high on the items of work they intend to perform first. Then, after skimming the cream, they have skipped out for South America, leaving their bondsmen or others to finish the work at a loss. This, however, is a very rare procedure nowadays.

You will see the necessity of having a record of contract prices not on one but on a number of different contracts, so that you may strike a fair average. I have found that the most convenient way of recording bids is to copy them from the lists given in the engineering journals, using an indexed note book. Under "Earth" I enter bids (high, low and average) for a few of the reservoirs let each year in different parts of the United States; I likewise record bids for sewer trenching, for railway earth work, for road earthwork, etc. And in this way, I keep also an up to date record of prices on concrete, masonry, piling, rock excavation, tunnels, etc. A section headed miscellanies is one that I oftenest consult. There I enter prices for sodding, clearing and grubbing, fencing, etc. You will have more luck than I have had if you find any printed information as to the actual cost of sodding, for example, and the same may be said of many another item. Contract prices are in such cases your only guide, and by all odds better than a guess; but if you were to trust to your memory or to an index to find them when you needed them, you would find your memory of little service and the ordinary indexes scarcely better.

I keep three sets of cost data note books. In one book, as I have just said, I enter contract prices; in another, I enter abstracts of actual cost of work given in published articles; and in the third book, I enter my own observations. I have done this now for some ten or more years, and I have never regretted the labor so spent. After all it takes but a small fraction of a day to keep the records up, when a system has once been worked out. Up to the present, there has been comparatively little published on the actual cost of engineering structures all told; and it is a curious fact that most of that which has been published relates to unusual or to difficult work. Thus I could refer you to a score of articles on the methods and cost of laying subaqueous water pipe for every single article on ordinary water pipe laying on land. I could give you references to forty different articles on the cost of tunnelling in rock, as published in one engineering journal, while during the same period of time that journal has not published one comprehensive article on open cut rock excavation or railroad work, and only one on rock trenching.

As to using cost data I need say but little. In making an estimate be liberal. Contingencies are almost certain to arise that you have not definitely forseen. Storms, strikes, delays in getting materials, errors of judgment as to materials to be encountered, or some others of a hundred and one things may act to increase the cost of the work. Therefore, I say, be liberal in your estimates. To add 5 or 10 or 15 per cent. for profit is seldom enough where much labor is involved; generally 20 or 25 per cent. makes a fair allowance for profits. One often hears it said that an over-estimate indicates as much ignorance as an under-estimate. Possibly it does, but I shall always prefer to be on the "over-estimate" side. I have never yet to hear a man complain because he had been called upon to pay less than he had expected to pay; but I do recall some very loud protests where the final bill exceeded the original estimate. So it is with companies, and with the public. They are more apt to regard the difference between your estimate and the actual cost as so much saved by your ability, rather than as so much erred in your estimate.

In closing, I would say that had this lecture been a written one I should have gained in conciseness, and I should have been enabled to present a larger number of facts; but after all, in an hour's time I could have given only a few data and they would

have been so dry as to be speedily forgotten. My principal object has been not to furnish you with data, but to assist you in forming the habit of collecting and analyzing cost data for yourselves. Perhaps a rather informal talk, illustrated with some personal examples, may have been more effective in attaining this end than a more formal lecture would have been in driving home the fact — that it pays to observe, to record, and to analyze costs; whether you are in civil or in mining engineering, as employees, or are yourselves employers.

THE DETAILED DESIGN OF A RAILROAD BRIDGE. PART II.

By W. H. BURR, C.E., AND M. S. FALK, C.E.

Art. 13. Specificatons for Lateral and Wind Bracing.

The following specifications apply to the bracing:

§ 30. Allowed unit stress, in tension, for longitudinal, lateral and sway bracing for wind and live load stresses = 18,000 pounds per sq. in.

§ 31. Angles subject to direct tension must be connected by both legs, or the section of one leg only will be considered as effective.

§ 33. Allowed unit stress, in compression, for lateral struts and rigid bracing = P = 13,000 — 70 l/r for wind stresses, where P, l, and r have the same meaning as previously. No compression member, however, shall have a length exceeding 125 times its least radius of gyration. Lateral struts, with adjustable bracing, will be proportioned by the above formula to resist the maximum due either to the wind and load or to an assumed initial stress of 10,000 pounds per sq. in. on all the rods attached to them.

§ 35. Members subjects to alternate stresses of tension and compression shall be proportioned to resist each kind of stress. Both of the stresses shall however be considered as increased by an amount equal to eight tenths of the least of the two stresses, for determining the sectional area by the above allowed unit stresses.

§ 37. The rivets in the lateral and sway bracing will be allowed 50 per cent. increase over usual allowed unit stresses.

§ 94. Where rods are used in the lateral, longitudinal or sway bracing, they shall be square bars, but in no case shall they have a less area than one square inch. Rods with bent eyes must not be used.

§ 95. All through bridges shall have latticed portals, of approved design, at each end of the span, connected rigidly to the end posts and top chords. They shall be as deep as the specified head room will allow.

§ 96. Where the height of the trusses exceeds 25 feet, an approved system of overhead diagonal bracings shall be attached to each post, and to the top lateral struts.

§ 97. All bars and rods in the web, lateral, longitudinal or sway systems, must be securely clamped at their intersections to prevent sagging and rattling.

ART. 14. DESIGN OF UPPER LONGITUDINAL WIND BRACING.

The tension members will be formed of angles connected by both legs, so that the full area will become available. The following table shows clearly the method of design, the allowable unit stress being 18,000 pounds per sq. in.:

Member.	Stress in Pounds	Area Required sq ins.	Section Adopted.	Gross Area of Section	Net Area of sec. in sq. ins.	Rivets Required at End.
U_1U_2	+42,500	2.36	1–3½ x 3½ x $\frac{7}{16}$″ angle.	2.88	2.50	6
U_2U_3	+33,000	1.84	1– " " $\frac{3}{8}$ "	2.50	2.17	5
U_3U_4	+23,700	1.33	1 " " " "	2.50	2.17	4
U_4U_5	+14,300	0.80	1– " " $\frac{5}{16}$ "	2.09	1.81	2
U_5U_6	+ 4,700	0.28	1– " " " "	2.09	1.81	1

These members are connected to the upper chord by $\frac{5}{8}$-inch gusset plates. The bearing capacity of one machine-driven rivet in this thickness of plate will therefore be 4,920 × 150 per cent. = 7,380 pounds, and this quantity determines the number of rivets required at the end connections as given in column 7, although all the connections will be made uniform with six rivets. The compression members at right angles to the axis of the bridge are not designed by any exact theory. They will be formed either of cross frames or struts, as indicated on the stress sheet, and they are more than ample in section to sustain the direct compressive stresses there indicated; in fact, since their

main duty is to stiffen the structure and to cause the two trusses to act as a whole, they are made as rigid as the judgment of the engineer requires. The portal bracing is designed in a somewhat similar way, although tested by computations in its various parts.

The struts will be placed at those points, U_4 and U where the upper chord is continued in a straight line, and where there are no inclined web members. They will be composed of four angles, each $3\frac{1}{2} \times 3\frac{1}{2} \times \frac{5}{16}$ inch, built up in I form with double lattice bars $2\frac{1}{4} \times \frac{3}{8}$-inch, and connected to two gusset plates, one lying on top of the cover plate of the upper chord and the other fastened to the bottom angle of the upper chord.

The cross frames will be placed at all the other panel points. They will be formed of an upper strut, like that just described, and a lower strut placed at the upper clearance limit and formed of four angles each $3\frac{1}{2} \times 3\frac{1}{2} \times \frac{5}{16}$ inch, latticed together in I form by bars $2\frac{1}{4} \times \frac{5}{16}$ inch. The lower strut will be fastened to the post by means of a $\frac{5}{16}$-inch gusset plate lying between two $3\frac{1}{2} \times 3 \times \frac{5}{16}$ inch angles, two feet long, the latter being riveted to the center of the post by 12 rivets. Between the two I struts will then be placed a compound lattice work composed of single $3\frac{1}{2} \times 3\frac{1}{2} \times \frac{5}{16}$-inch angles tied together at intersections by small square plates with five rivets at each crossing and fastened to the struts by $\frac{5}{16}$-inch gusset plates, the details of which are shown in Plate II. The cross frames are really the intermediate transverse bracing, the theory of whose design would be determinate if it were not the duty of the upper horizontal lateral bracing to transfer all the wind load to the upper ends of the end posts. It is possible to design the cross frames by ignoring this upper wind bracing. Their main function however, is to stiffen the bridge under rapidly moving train loads, rather than to give additional stability against wind loads.

Art. 15. Design of Portal Bracing.

The portal bracing will be made as rigid as possible and will take the form of a latticed girder placed in the plane of the pins of the end posts, as shown in outline on the stress sheet. The upper and lower flanges will be made alike of two $6 \times 4 \times \frac{3}{8}$-inch angles with a $14 \times \frac{3}{8}$-inch web plate. The two flanges will be tied together by a compound latticing composed of single $5 \times 3\frac{1}{2} \times \frac{3}{8}$-inch angles. The upper flange will be fastened to the cover plate

of the top chord, U_1U_2, by means of a bent gusset plate, as shown in Plate II.; the lower flange will be fastened to the side plate of the end post in a manner similar to that of the cross frames. The lower flange will, moreover, be strengthened at each end connection by means of a plate and angle bracket, composed of a $\frac{5}{8}$-inch plate and $3\frac{1}{2} \times 3\frac{1}{2} \times \frac{5}{8}$-inch angles, as shown in Plate II. The outer end of the bracket will be supported from the latticing of the portal frame by a single $3\frac{1}{2} \times 2\frac{1}{2} \times \frac{5}{8}$-inch angle.

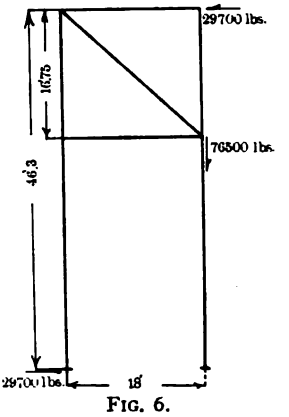


FIG. 6.

The wind force acting at the upper end of the end post is 29,700 pounds. The length of the end post is 46.3 feet, and the distance between trusses 18 feet. The increase of load on one truss, which acts as if hung at the connection point of the lower flange of the portal, will therefore be 76,500 pounds. The multiple bracing employed produces ambiguity in the stresses of the portal members. If the assumption be made, as shown in the accompanying figure, that the multiple bracing is replaced by a single tension-bar, and that the wind reaction is entirely resisted at the foot of the leeward post, the stress in the lower flange will be: $\frac{76,500 \times 18}{16.75} = 82,200$ pounds compression. The allowed intensity of stress is $P = 13,000 - 70\, l/r$, in which $l = 216$ inches and r may be taken approximately as 3 inches. Then $P = 8,000$ pounds per sq. in., approximately, and the sectional area required will be $\frac{82,200}{8,000} = 10.4$ sq. ins.

The actual area will be:

2	$6 \times 4 \times \frac{3}{8}$-inch angles	$= 7.22$ sq. ins.
1	$14 \times \frac{3}{8}$-inch plate,	$= 5.25$ " "
		12.47 sq. ins.

The section adopted is therefore sufficient.

The stress in the upper flange may be taken to be equal to the

wind reaction transmitted from one truss to the other; its section, although so taken, need not be as great as that of the lower flange.

ART. 16. DESIGN OF LOWER LONGITUDINAL WIND BRACING.

Although the inclined web members in this horizontal truss may suffer apparently reversal of stress, it must be remembered that the two systems of bracing provide for opposite directions of the wind without such reversal. The specifications in regard to reversal of stresses do not therefore become operative. If it be assumed that the inclined web members act in compression, they must be designed with the prescribed unit compressive stresses. As they are fastened at two points to the stringers and at the center to each other, it may be proper also to assume the effective length of a member to be the distance from its end to the point of intersection with the center line of the stringer, *i. e.*, in this case about 120 inches. These members will be formed of two unequal legged angles, with the longer legs vertical and riveted back to back. The following table shows the sections adopted:

Member.	Stress in Pounds. Compression.	Radius of Gyration in ins. Final Section.	Allowed Unit Stress in lbs. per sq. in.	Area Required in sq. ins.	Section Adopted. 2 Angles	Actual Section in sq. ins.	Number of Rivets Required at End Connection.
L_0L_1	71,600	1.56	7610	9.4	5x4x$\frac{9}{16}$"	9.52	14
L_1L_2	59,200	1.56	7610	7.8	" " $\frac{1}{2}$	8.58	11
L_2L_3	47,700	1.56	7610	6.3	" " $\frac{3}{8}$	6.46	10
L_3L_4	36,900	1.56	7610	4.85	" " "	6.46	7
L_4L_5	26,800	1.23	6170	4.35	4x4x$\frac{3}{8}$	5.7	6
L_5L_6	17,500	1.23	6170	2.84	" " "	5.7	4

It will be seen that the sections adopted for the panels near the center of span are greater than actually needed; but since a portion of the duty of these members is to stiffen the structure under rapidly moving loads their section may properly be greater than required by the computed stresses.

The connection of these members to the posts is made by a flat plate, $\frac{1}{2}$ inch thick, which in turn is fastened to the foot of the post by $3\frac{1}{2} \times 3\frac{1}{2} \times \frac{3}{8}$-inch angles, as shown in Plate II. The amount of stress which these angles must carry to the plate is the difference of wind stresses found in the two adjacent lower chord panels which has a maximum value of 222,000 — 122,000 = 100,000 pounds at the foot of U_1L_1.

The specifications for wind bracing riveting show the single

shearing capacity of one rivet to be 5,410 × 150 per cent. × ⅔ = 5,410 pounds, and the bearing capacity in a ⅜-inch thickness of metal to be 4,920 × 150 per cent. × ⅔ = 4,920 pounds. At the foot of U_1L_1 there will therefore be required $\frac{100,000}{4920} = 21$ rivets; since the two angles inside the post do not afford space for all these rivets, a U-shaped plate will be riveted within the post, which will permit placing the required number of rivets. At the foot of U_2L_2, the maximum stresses carried by the plate will be 78,000 pounds, and will require 16 rivets. At the foot of U_3L_3, the stress will be 56,000 pounds, and 12 rivets are required. Plate II. shows the disposition of these rivets in the angles. The number of rivets connecting the ends of the lateral bracing to the plate, as given in column 8 of the above table, was found in the same way as for the upper chord.

The lower flanges of the floor beams act as struts in the lower lateral system. The ½-inch plate which is used as a connection at the foot of the posts, is sufficiently extended to be firmly riveted to the lower flange of the beam. The number of rivets necessary may be determined by assuming that the plate transmits to the floor beam that component of the stress in the inclined lateral members which acts in a direction at right angles to the axis of the chords.

ART. 17. DESIGN OF BED PLATES, FRICTION ROLLERS AND PEDESTALS.

§ *100. All bed plates must be of such dimensions that the greatest pressure upon the masonry shall not exceed 250 pounds per sq. in.*

§ *101. All bridges over 75 ft. span shall have at one end nests of turned friction rollers running between planed surfaces. These rollers shall not be less than 2⅞ inches diameter for spans 100 feet or less, and for greater spans this diameter shall be increased in proportion of 1 inch for 100 feet additional.*

The rollers shall be so proportioned that the pressure per linear inch shall not exceed the product of the diameter in inches by 300 pounds.

§ *104. Pedestals shall be made of riveted plates and angles. All bearing surfaces of the base plates and vertical webs must be planed. The vertical webs must be secured to the web by angles having two rows of rivets in the vertical legs. No base plate or web connecting*

angle shall be less in thickness than ¾ inch. The vertical webs shall be of sufficient height, and must contain material and rivets enough to practically distribute the loads over the bearings or rollers.

Where the size of the pedestal permits the vertical webs must be rigidly connected transversely.

§ *105. All the bed plates and bearings under fixed and movable ends must be fox bolted to the masonry; for trusses, these bolts must not be less than 1¼ inches diameter.*

The dead load reaction at the base plate is 325,000 pounds, and the live load 420,000 pounds; a total of 745,000 pounds. The masonry bearing will be $\frac{745{,}000}{250} = 2{,}980$ square inches. The diameter of the rollers according to the specification should be at least $2\frac{7}{8} + \frac{250}{100} = 5\frac{3}{8}$ inches, but since it is better practice to build segmental rollers the diameter of these rollers may be taken at 8 inches. Assuming then that eight rollers will furnish a proper form of distribution, the number of linear inches of length per roller required will be $\frac{745{,}000}{8 \times 300 \times 8} = 38.9$ inches; the rockers will therefore be 8 in number, 8 inches high, 5 inches wide and 4 feet 5 inches long, rolling on a base plate 1¼ inches thick, 4 feet 2 inches × 5 feet 6 inches in area. A 1¼-inch plate, 50 inches × 4 feet 6 inches, placed over the rockers, will form the seat or bed plate for the pedestal proper. Both base plate and bed plate will have riveted to them, so placed as to be directly below the center of the end post, a flat bar, 2¼ inches × ⅜ inch × 4 feet 2 inches long, made to fit corresponding grooves turned in the rockers to prevent all lateral motion of the rockers or pedestal. The rollers will be fastened rigidly together in their proper positions with ⅜-inch clear spacing by a ¾-inch strap on each side 2 feet 3 inches long secured to the axis of each roller by a nut.

The pedestal must distribute uniformly to the shoe or bed plate the vertical load carried by the pin at the foot of the end post. For this reason it should be made deep enough to prevent appreciable deflection, but not so deep as to cause a tendency to buckle the side plates. A completely rational design for a pedestal is practically impossible. It is treated in some cases as a short plate girder uniformly supported along the bottom and carrying a concentrated

load at its center. It is more usual to select some tried form of pedestal and adapt it for use in accordance with good judgment; this will be done in the present case. The side plates of the pedestal supporting the end pin must first be considered. The diameter of this pin should therefore be known, and in this instance may be assumed to be 7 inches. With an allowable bearing pressure of 15,000 pounds per square inch, the total thickness of the side plates for one half of one pedestal will be $745{,}000/2 \div (15{,}000 \times 7) = 3.55$ inches. If the main side plates are fastened between two $6 \times 6 \times \frac{8}{4}$ inch angles, $\frac{8}{4}$ filling plates will be required above the angles. In addition to these two $\frac{8}{4}$ inch plates there will then be needed two $\frac{11}{16}$ inch plates and one $\frac{8}{4}$ inch plate, giving a total thickness of $3\frac{5}{8}$ inches. An additional plate $\frac{7}{16}$ inch thick, called a lap plate, projecting upwards within the end post, will be fastened to the inside of these plates. The riveting of these connections is clearly shown in Plate II. It will be seen that a $\frac{7}{16}$-inch cover plate and two $3\frac{1}{2} \times 3\frac{1}{2} \times \frac{8}{8}$ inch angles are added to the upper edges of the pedestal in order to make it conform in finished appearance to the end post.

The pedestal at the fixed end of the truss will be exactly similar to the one above described, but the rollers will be dispensed with and the difference in height will be provided for in the pedestal itself.

The base plate, as shown in the figure, will be rigidly secured to the masonry by 1½-inch anchor bolts 2 feet long. On the outer side of the rollers, a dust guard of two angles and a plate built in Z-shape will be connected to the anchor bolts.

ART. 18. DESIGN OF END FLOOR BEAM.

The end floor beam, which is fastened to the shoe plate and which carries not only the end stringers, but also the short cantilever brackets supporting the track from the abutment itself to the end stringer, still remains to be designed.

The end shear of this floor beam will be the live load shear of a single stringer, 62,500 pounds, together with an estimated dead load shear of 7,500 pounds, or a total of 70,000 pounds. The maximum moment will then be 70,000 pounds × 63 ins. = 4,440,000 inch pounds. Assuming the effective depth of girder to be 54 inches, the required sectional area of one flange will be 8.15 square inches and it may be composed of two angles $6 \times 4 \times \frac{1}{2}$ inch with

a gross section of 9.6 square inches and a net section of 8.6 square inches.

The web will be a 55¾ × ⅜-inch plate with an area of 20.9 square inches. Allowing a compressive intensity stress of 8,000 pounds per square inch in the end stiffeners, the area required will be 8.75 square inches. Two 6×4×½-inch angles having an area of 9.5 square inches will be used, with fillers.

The end floor beam rests on and is riveted to a horizontal ½-inch plate, which in turn is solidly united to the shoe plate. To prevent lateral deflection, the upper flange of this floor beam is tied to the end post by means of a horizontal bent plate, and in addition a vertical triangular shaped plate is fastened to the end stiffeners and to the shoe plates, as shown clearly by Plate II. The plane of the lower lateral bracing does not coincide with the plane of the shoe plate, and to provide a proper connection, two 6 × 4 × ½-inch angles are riveted to the web of the floor beam at the proper elevation.

The end stringer bracket is also shown in sufficient detail in Plate II. The floor beam is slotted in order to allow the tie plate forming the cover plate of the bracket to pass through it. This tie plate is riveted to the upper flange of the adjacent intermediate stringer, to relieve as much as possible the direct stress of tension which may come upon the rivet heads connecting the bracket to the floor beam.

Art. 19. Design of Pins and Joint Details.

§ 38. Pins shall be proportioned so that the shearing stress shall not exceed 9,000 pounds per square inch; nor the crushing stress on the projected area of the semi-intrados of any member (other than forged eye-bars, see § 80) connected to the pin, be greater per square inch than 15,000 pounds; nor the bending stress exceed 18,000 pounds, when the applied forces are considered as uniformly distributed over the middle half of the bearing of each member.

§ 78. The lower chord shall be packed as narrow as possible.

§ 80. The diameter of the pin shall not be less than ¾ the largest dimension of any eye-bar attached to it. The several members*

*The following analysis furnishes the foundation for this specification. If the width of an eye-bar be represented by w, and the depth by h (the thickness of the head is taken the same as that of the bar) and if T be the permissible intensity of tensile stress, the total stress carried by the bar will be $w.\ h.\ T.$ If the diameter of the

attaching to the pin shall be so packed as to produce the least bending moment upon the pin, and all vacant spaces must be filled with wrought filling rings.

§ 88. Where necessary, pin holes shall be reinforced by plates, some of which must be of the full width of the member, so that the allowed pressure on the pins shall not be exceeded, and so that the stresses shall be properly distributed over the full cross-section of the members. These reinforcing plates must contain enough rivets to transfer their proportion of the bearing pressure, and at least one plate on each side shall extend not less than 6 inches beyond the edge of the bottom plates (§ 87).

§ 87. The open sides of all compression members shall be stayed by batten plates at the ends. . . . The batten plates must be placed as near the ends as practicable, and shall have a length not less than the greatest width of the member or 1½ times its least width.

§ 89. Where the ends of compression members are forked to connect to the pins, the aggregate compressive strength of these forked ends must equal the compressive strength of the body of the members.

In addition to these direct specifications the following may be noted:

§ 60. In compression members, abutting joints with planed faces must be sufficiently spliced to maintain the parts accurately in contact against all tendencies to displacement.

§ 61. In compression members, abutting joints with untooled faces must be fully spliced, as no reliance will be placed on such abutting joints. . . .

The bending in pins and the allowed bearing of the plates on pins are peculiarly related; the larger the diameter of the pin, the narrower are the necessary bearing surfaces and consequently the smaller are the bending moments. If the diameter of the pin be decreased, the bearing surfaces must be increased in width. In that case the bending moments are increased and the pin diameter

pin be represented by d and C be the permissible bearing intensity of stress on the pin, then $d.\ w.\ C$ will represent the bearing allowed on the pin. The two quantities $w.\ h.\ T$ and $d.\ w.\ C$ should be equal; if the ratio of C/T be taken at 4/3, then $wh\,T = dwC$ and $d = 3/4h$.

may have to be increased. It will usually be impossible to obtain an economical balance for these conflicting conditions throughout the truss without many different sizes of pin. It is therefore customary to fix upon one size of pin for the lower chord, and another smaller one for the upper chord, then test them for bending and design the bearing surfaces to correspond with the diameters so chosen. The packing or arranging of the eye bars must be so chosen as to reduce the bending to a safe minimum.

Specification § 80 at once fixes a minimum limit for the size of the lower chord pins and also of the pins at the upper extremity of the end post to 6 inches; and the pins in the upper chord to $5\frac{1}{4}$ inches. The sizes tentatively assumed will be 7 inches for the first set of pins and 6 inches for the latter. The bearings of the various members for these sizes of pins are then designed, and then all the members at any one point so packed as to produce the least practicable bending moment. The "play" or spacing allowed in packing eye-bar heads may sometimes be taken as small as $\frac{1}{32}$ inch to allow for slight imperfections in manufacture, but it is usually taken as $\frac{1}{8}$ inch for each eye-bar head. This amount may be increased to meet the requirements of any special case. The clear distance between built members such as chords or posts is usually greater; it may be taken as high as 1 inch. It will be found necessary at some connecting points to cut away parts of the flanges of channels or angles in built-up members on account of the interference of inclined members. If this must be done, the remaining part of the member must always be tested by computation as to its strength, considering it as a short piece in compression. In most cases the usual pin bearing plates are sufficient to replace the metal cut away. The following formula * has been much used for the purpose of designing such forked portions of the ends of posts:

$$t = \frac{P}{8000b} + \frac{l}{27}, \qquad \text{Eq. (1)}$$

in which t represents the total thickness of metal whose width is b; P the total load on one jaw of the post (usually one half the total load carried by the post or column) and l the distance from the center of the pin hole to the last center line of rivets in the body of the column back of the cut in the angle or in the flange of the channel. This formula is applicable to steel with ultimate

[1] See Burr's "Resistance of Materials," page 515.

tensile resistance running from 60,000 to 68,000 pounds per square inch. For higher steel, or for highway bridges, or for other structures where less margin of safety may be justifiable, the value of t may be made correspondingly less than given by Eq. (1).

Pin Plates in Posts.

The posts at their lower extremities carry to the pins not only their maximum stresses as members of the truss but also the compression due to their acting as supporting struts for the floor beams. It is possible and it should be assumed that the maximum post stress and the greatest panel load occur together. In the present case this requires that the lower ends of the posts be reinforced with sufficient thickness of bearing plates to carry 98,000 pounds in addition to the stress taken from the stress sheet (Plate I.). In order that this floor beam load may be distributed uniformly to the pin by both jaws of the column, it is necessary that the two sides of the post be riveted firmly together to act as a whole; otherwise the inside jaw will carry the greater portion of the load. This is usually accomplished by inserting between the two parts of the column, at the end of the floor beam, a diaphragm which acts as a continuation of the web plate of the beam. This diaphragm will be composed of a $\frac{3}{8}$-inch plate riveted between four $4 \times 3 \times \frac{3}{8}$-inch angles. The method of fastening is clearly shown in Plate II.

Member L_1U_1 — Lower End.

This member needs to be fastened at its lower end only to increase the general stiffness of the structure, since it is simply a hanger to carry load to the upper panel point. The U-shaped plate to which the lower lateral bracing is attached furnishes inside pin plates, but in addition two $\frac{3}{8}$-inch plates will be fastened to the outside extending upwards to the bottom of the floor beam, so that the latter may have support during erection.

Member L_1U_1 — Upper End.

A 1-inch plate, bearing on a 7-inch pin, may carry 105,000 pounds. The load to be carried at this point is 117,000 pounds; therefore 1.12 inch total width of bearing will be required. As the webs of the channel are each 0.375 inch thick the thickness of pin plate required would be 0.37 inch, but since the net section of the channels is reduced by the diameter of the pin, it will be advisable to use two $\frac{5}{8}$-inch pin plates, especially as the vertical dis-

tance from the top of the pin to the upper extremity of the channels is but 6 inches. The net section through this point should not be less than $\frac{2}{3}$ of the transverse net section, and the $\frac{5}{8}$-inch pin plates chosen will satisfy the condition.

Since the allowable stress in the main section is 6,000 pounds per sq. in., each pin plate may be supposed to carry $15 \times \frac{5}{8} \times 6{,}000 = 56{,}300$ pounds, and as the rivet bearing in a $\frac{5}{8}$-inch plate is 4,920 pounds, 12 rivets will be required.

Member U_2L_2 — Lower End.

The sum of the dead and live loads carried at this point, together with the floor beam load of 98,000 pounds, may produce a total load of 357,000 pounds, or 178,500 pounds on each jaw of the post resting on a 7-inch pin. A total thickness of $\frac{178{,}500}{105{,}000} = 1.7$ inches will therefore be required. A $\frac{5}{8}$-inch inside, and a $\frac{5}{8}$-inch outside pin plate, together with the $\frac{9}{16}$-inch main plate, give a thickness of 1.81 inches, and will prove satisfactory.

Since the bearing value for one rivet in a $\frac{9}{16}$-inch plate is 7,380 pounds, or less than the double shear value, the former quantity will determine the number of rivets. It may be assumed that the total stresses carried by the different plates are proportional to their thickness; therefore $(\frac{5}{8} + \frac{5}{8}) \div 1\frac{9}{16} = 69\%$ of the total stress must be transferred by rivets from the main plate to the pin plates. In this case $0.69 \times 178{,}500 = 123{,}000$ pounds; therefore at least 17 rivets will be required; Plate II. shows the arrangement of plates and rivets.

Member U_2L_2 — Upper End.

The 6-inch pin at this point will carry a bearing pressure of 90,000 pounds per inch width of plate, the load on each jaw of this post being 129,500 pounds. 1.44 inches thickness of bearing will be required, and this thickness will be afforded by the $\frac{9}{16}$-inch main plate, with a $\frac{7}{16}$-inch outside and a $\frac{1}{2}$-inch inside pin plate. The bearing value of one rivet in a $\frac{9}{16}$-inch plate is 7,380 pounds, and the rivets transfer 63 per cent. of $129{,}500 = 81{,}500$ pounds, to the pin plates, hence the required number will be 11. Plate II. shows the arrangement adopted.

Member U_3L_3 — Lower End.

The load carried by one jaw resting on the 7-inch pin, including the floor beam load, will be 101,500 pounds and the thickness

required will be $\frac{101500}{100000} = 0.97$ inch. A $\frac{5}{8}$-inch pin plate in addition to the $\frac{3}{8}$-inch web of the channel will therefore suffice. The stress transferred to the pin plate will be 63,500 pounds and as the bearing value of one rivet in a $\frac{3}{8}$-inch plate is 4,920 pounds, 13 rivets will be required.

Member U_3L_3 — Upper End.

The thickness of plates for one jaw bearing on a 6-inch pin will be $\frac{52500}{90000} = 0.58$ inches. A $\frac{1}{2}$-inch pin plate will be riveted to the outside of the channel and the number of rivets required will be 6.

It will not be necessary to repeat these operations in detail for the other posts of this truss, the method of design being precisely the same as those already given.

ART. 20. DESIGN OF PIN CONNECTIONS OF UPPER CHORD MEMBERS.

As the joint of two adjoining upper chord members having different inclinations is always at the angle in the chord with its plane passing through the axis of the pin, it is usually made abutting and riveted so as to make the chord continuous. This makes the chord stiffer than if the joints were pin bearing. It has become almost the invariable practice, however, to make the joint at the top of the end post an open pin bearing one. Since all abutting faces will be planed, specification § 60 requires no splice plates except those sufficient to prevent displacement. The only stress transferred from a pin to a chord member will then be the resultant, in the direction of the chord member, of the maximum stresses in the web members meeting at that point, *i. e.*, the increment of stress. Sufficient pin-bearing area must be provided to carry this increment of stress.

The joint for adjoining chord members whose axes are in the same straight line is never made at a pin, but at some distance from it, on that side away from the center. This procedure is adopted for convenience in erection which usually proceeds from the center towards the ends. This joint is placed as near the pin as practicable, and in a chord 20 inches deep, it is usual to have three rows of rivets in the splice plate on each side of the joint; for splices in chords 24 to 30 inches deep 4 rows are usually inserted.

At such a joint the batten plate on the bottom and a short cover plate on top are used to strengthen the splice.

It has already been noted that the axes of the pins have been placed 14½ inches below the edge of the cover plate, or 0.7 inch below the center of gravity of the chord section. This tends in some degree to neutralize the flexure due to own weight by the counter flexure introduced by the increment of chord stress.

In the bridge under consideration no joint will be made at panel points U_4 and U_6; the members $U_5U_4U_5$ and $U_5U_6U_5$ will each be made in single pieces about 59 feet long, which is entirely practicable. The supporting struts which frame into these members at their center points are connected by means of angles, as shown in Plate II. The joint for U_2 is made 2 feet 4½ inches away from the center of U_2 and $\frac{7}{16}$-inch splice plates will be riveted on the inside of the side plates of the chord, with 4 rows of rivets on each side of the joint. A ⅛-inch filler is necessary to allow for the difference in thickness of plates in the two chord members. The ½-inch outside plate will be continued to cover the joint.

The maximum increment of stress in U_2U_3 given by the web member at U_2 is 140,000 pounds, or 70,000 pounds for each jaw, The 6-inch pin can transfer this stress to the $\frac{13}{16}$-inch side plate, but for increased stiffness and solidity a ½-inch plate with ½-inch filler will be riveted on the outside of each jaw. As may be observed, all connections are made so strong that a member should fail rather in its body than at its end connections.

Connection at U_3.

The maximum increment of stress for the member U_3U_4 at panel U_3 in the direction of the axis of U_3U_4 is found graphically from the stresses in the web members to be 200,000 pounds. The thickness of each jaw bearing on a 6-inch pin must then be at least 1.1 inches. It will be seen in Fig. 7 that besides the $\frac{9}{16}$-inch filler plate and the ⅜-inch lap plate, a ⅜-inch inside and a ⅜-inch outside pin plate have been used. This is more than the computations require, but not more than desirable for the stiffness of the continuous upper chord.

Plates corresponding to those riveted to U_3U_4 are fastened to U_2U_3 at U_3. The outside edges of the main side plates of adjacent members should always be in line. In this truss the uniform distance from back to back of these plates is 23 inches. The abutting pieces at U_3 are shown in Fig. 7.

The stress carried by each plate will be determined by multiplying its thickness in inches by the allowed bearing of a 1-inch plate on a 6-inch pin, and this quantity determines the number of rivets required in each plate. These rivets must be designed not only for single shear for each separate plate, but also for the combined bearing of the outside plates on the main inside web plate. Where field rivets are used their stress value is only two thirds that of shop rivets.

If the thickness of pin plates is large, considerable bending, indeterminate in amount, may take place in the rivets, and it is proper

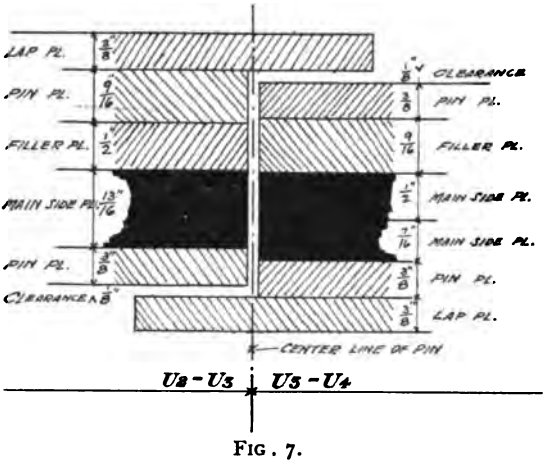


FIG. 7.

on this account to add more rivets than those actually required by computation. Moreover, since the cover plate and top angles of the chord section receive their stress cumulatively, the pin plates which transfer a part of the stress to them should be made long enough to enable this stress to be transferred directly, instead of first passing through the main web plate.

Since there is thus a certain amount of indetermination in the transmission of stress in an abutting joint, such a joint is not designed strictly according to computations, but more or less according to experience tempered by the engineer's judgment. The design adopted must, however, always be tested by some method of analysis to determine its safety.

Connection at U_5.

The pin plates at this panel point are designed in a manner similar to that followed for U_3. The design adopted, Plate II., provides abundant material.

ART. 21. DESIGN OF DETAILS AT ENDS OF END POST.

Lower Extremity.

The end connections of L_0U_1 are not abutting, but pin bearing. Hence all the stress in L_0U_1, 899,000 pounds, is transferred to the pin, and from that to the pedestal plates.

A 1-inch plate bearing on a 7-inch pin can carry $7 \times 15{,}000 = 105{,}000$ pounds; therefore a 4.28-inch thickness of pin plate is required for each jaw. There will then be added to the main web plates $\frac{1}{2}$ inch and $\frac{7}{16}$ inch thick respectively, an outside $\frac{5}{8}$-inch lap plate, a $\frac{5}{8}$-inch plate below this and a $\frac{9}{16}$-inch plate over a $\frac{1}{2}$-inch filler. On the inside, next to the side plate, there will be a $\frac{9}{16}$-inch plate and then a $\frac{7}{16}$-inch plate; this gives a bearing thickness of $4\frac{1}{2}$ inches. The following rivets will be required in single shear for the various plates; Plate II. shows their distribution:

Outside Plates.		Inside Plates.	
$\frac{5}{8}$-inch lap plate	12 rivets.	$\frac{7}{16}$-inch plate	9 rivets.
$\frac{5}{8}$-inch plate	12 "		
$\frac{9}{16}$-inch "	11 "	$\frac{9}{16}$-inch plate	11 "
$\frac{1}{2}$-inch "	10 "		

Upper Extremity.

The same thickness of $4\frac{1}{2}$ inches of pin plate is required at the upper extremity as at the lower, but a portion of this thickness will be formed of an inside diaphragm, partly to avoid the inside pin plates interfering with the web members, and partly for the sake of the additional stiffness gained by this form of connection.

The diaphragm will be composed of a $\frac{11}{16}$-inch web, with four $4 \times 3\frac{1}{2} \times \frac{1}{2}$-inch angles built in the form of a vertical I. Two $\frac{1}{2}$-inch fillers and two $\frac{9}{16}$-inch plates will be added to the diaphragm to bear on the pin. Fig. 8 shows clearly the dimensions of the pin plates fastened to the side plates. The computations need not be repeated here, it being remembered that one half the diaphragm plate thickness should be included in the thickness of one jaw.

End Connection of U_1U_2.

The connection of U_1U_2 at U_1 is designed in precisely the same manner as the end post connection at U_1. The stress in one jaw is 429,000 pounds, and 4.1 inches is the thickness of pin plates required. An inside diaphragm will again be used and Fig. 8 shows clearly the sections adopted.

Since the end post and U_1U_2 are not riveted together it is usual to allow a small clearance between them for ease in erection. Fig. 8 shows the clearance adopted.

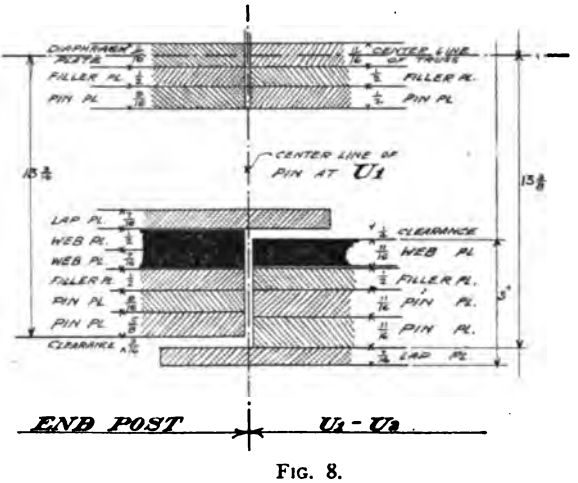


FIG. 8.

It will be seen that open joints are subject to a better defined analysis than abutting joints, but they form a heavier, more cumbersome and less rigid connection.

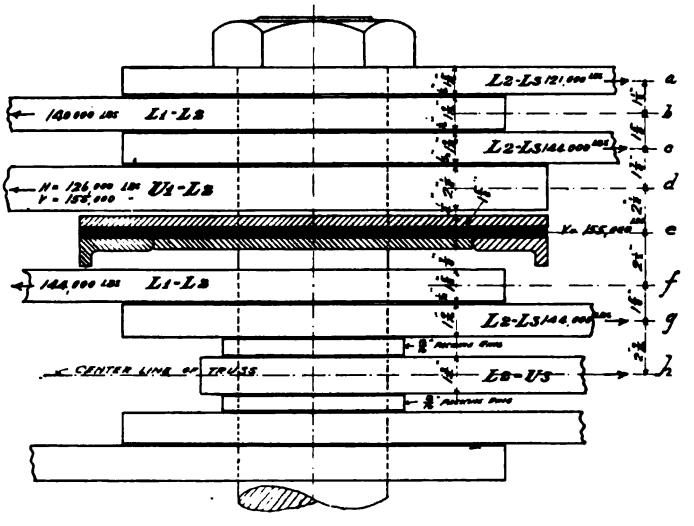
ART. 22. BENDING OF PINS.

Lower Chord Packing.

Panel Point L_2.

The packing of pin L_2 and the computations of the bending moments in it will furnish characteristic operations typical of all other cases. Fig. 9 shows the disposition of the members meeting at L_2, the clearances, and distances between centers of adjacent pieces and the stresses carried by the pieces when L_1L_2 has its maximum stress. The maximum stresses in all the members meeting at one point are not concurrent since they are caused by different positions of the moving load. It becomes necessary to test each pin, (1) with the maximum stresses existing in the web members, and (2) with the maximum stresses existing in the chord members. (It is sufficiently accurate to assume that the same position of loading causes the maximum stresses in the two

adjacent chord members or in the web members converging on the pin.) As a rule, the greatest pin bending in the lower chord occurs with the greatest chord stresses, and in the upper chord with the greatest web stresses.



7" PIN AT L2

FIG. 9.

The wind load stresses in the lower chord may be neglected as a factor in producing bending in the pins.

Taking moments about the center of each piece in turn there is found:

	Horizontal Moment.	Vertical Moment.
About *b*	+ 181,500 in. lbs.	
" *c*	+ 151,000 " "	
" *d*	+ 385,000 " "	
" *e*	+ 383,000 " "	330,000 in. lbs.
" *f*	+ 380,000 " "	330,000 " "
" *g*	+ 144,000 " "	

The maximum moment, therefore, occurs at *e* and is equal to

$$\sqrt{383{,}000^2 + 330{,}000^2} = 505{,}000 \text{ inch pounds.}$$

The allowed unit bending stress is 18,000 pounds per sq. in., and the bending resistance of a 7-inch pin is 606,100 inch pounds The packing at this point is, therefore, satisfactory.

If the bending be computed when L_2U_1 has its maximum stress, the vertical component of which is 166,000 pounds, it is seen that the vertical moment would be increased slightly, but the horizontal moment would be more than correspondingly decreased. The maximum bending moment on the pin occurs in this case, therefore, with the maximum chord stress.

Other panel points in the lower chord are treated in precisely the same manner; Plate II. shows the packing employed.

Upper Chord Packing.

The packing at panel point U_3 may be assumed characteristic of the entire upper chord; Fig. 10 shows clearly the spacing and also the stresses in the different parts, when U_3M_4 takes its maximum stress. Since the two chord members U_2U_3 and U_3U_4 are

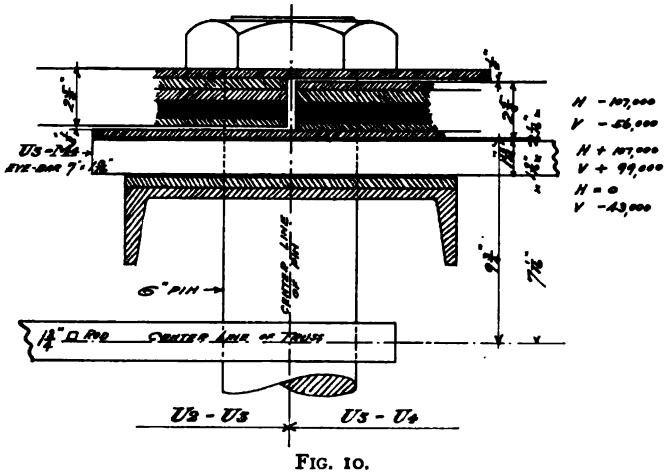


FIG. 10.

abutting and as there is practically no eccentricity between them, the resultant stress in the web members U_3L_3 and U_3M_4 is entirely resisted by U_3U_4, the horizontal and vertical components of which are easily found graphically.

The maximum stress in U_3M_4 is + 294,000 pounds, and the concurrent stress in U_3L_3 is — 86,000 pounds.

The side plates of the chord form the supports of the ends of the pin, the center of the supporting forces being at the center of the plates, as shown in Fig. 10. The members causing the bending in the pin are U_3M_4 and U_3L_3, the stress in the latter, — 86,000

pounds, being wholly vertical. The horizontal and vertical components of the stress in one half of U_2M_4 are:

H. = + 107,000 lbs.
V. = + 99,000 "

Fig. 10 shows that the bending moment in the central portion of the pin is then composed of

Hor. Mom. = $107{,}000 \times 2\frac{1}{16} = 221{,}000$ inch pounds.
Vert. " = $99{,}000 \times 2\frac{1}{16} - 43{,}000 \times 3\frac{5}{8} = 48{,}000$ inch pounds.

Hence the resultant moment is:

$$\sqrt{221{,}000^2 + 48{,}000^2} = 226{,}000 \text{ inch pounds.}$$

The allowed bending resistance of a 6-inch pin is 318,000 inch pounds. A 6-inch pin is therefore satisfactory at U_2.

Other upper chord panel points are investigated in exactly the same manner. It is desirable to repeat the operations in detail for

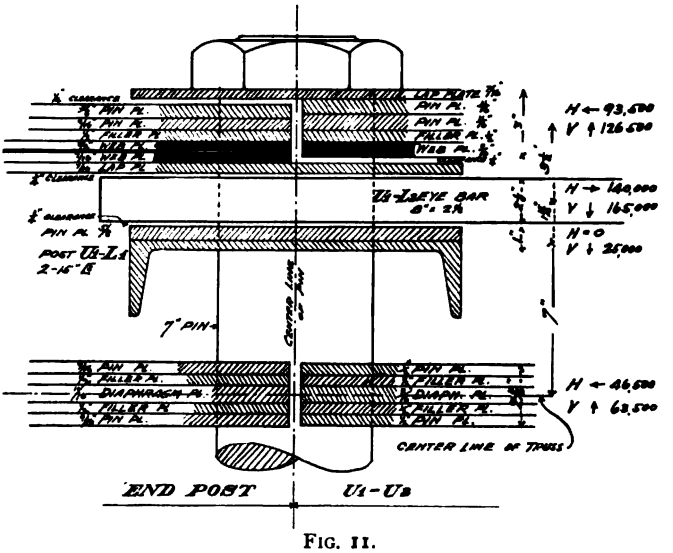


FIG. 11.

that panel point only at the upper extremity of the end posts (Fig. 11), and this point will be investigated for that position of loading which causes the maximum stress in U_1L_2 and the following table shows the components of the direct stresses in the members meeting at U_1 for that condition of loading:

	Vertical Components.	Horizontal Components
U_1L_1	+ 50,000 pounds.	——
L_0U_1	—620,000 "	—510,000 pounds.
U_1U_2	+240,000 "	+790,000 "
U_1L_2	+330,000 "	—280,000 "

No essential error will be introduced if it be assumed that there is no eccentricity in the line of action of L_0U_1 (the end-post) and U_1U_2. The resulting differences between their stresses may therefore be taken exactly along their center lines; a part of this stress is carried by the diaphragm, in this case about 34 per cent. Fig. 11 shows the stresses carried at one half of the panel point.

The resultant moments in inch pounds are as follows:

Center of Moments at Center of	Horizontal Moment.	Vertical Moment.	Maximum Moment.
U_1L_2	← 306,000	↑ 415,000	515,000
U_1L_1	← 222,500	↑ 345,000	
center line of truss.	→ 103,500	↓ 99,500	

The allowed bending resistance of a 7-inch pin is 606, 100 inch-pounds; and therefore satisfies the requirements at U_1.

Art. 23. Camber.

§ 107. *All bridges shall be cambered by giving the panels of the top chord an excess of length in the proportion of $\frac{1}{8}$ inch to every 10 feet.*

In accordance with this specification the following table shows the original lengths and the changed lengths of the upper chord members. It is seen that the end post is not changed in length.

	Original Length.	Changed Length.
L_0U_1	46′ 4″	46′ 4″
U_1U_2	39′ $6\frac{9}{32}$″	30′ $6\frac{5}{8}$″
U_2U_3	"	"
U_3U_4	29′ $6\frac{1}{8}$″	29′ $6\frac{1}{2}$″
U_4U_5	"	"
U_5U_6	29′ 2″	29′ $2\frac{3}{8}$″

No changes are made in the lengths of the main web members, their final lengths being the same as if no changes had been made in the lengths of the upper chord members.

The stretching of the lower chord panels makes it necessary to increase the lengths of M_3M_4 and M_5M_6 to an amount equal to half that stretch. The final length of each of these members will then be 29 feet $2\frac{3}{16}$ inches.

ART. 24. CONCLUSION.

The principles outlined indicate a system of rational treatment for the design of all parts of a modern truss bridge. It is obvious that a wide range of treatment of details is permissible in securing the above results, and those given here are subject to this general observation. Other details of equal efficiency might be designed but those given are at least as effective as others which might have been used and have served the purpose of illustration at least as well.

A carefully made bill of materials with the resulting computation of weights would show that the total shipping weight of this 350-ft. single track through span would be 821,000 pounds.

NOTES ON METALLOGRAPHY.

BY WILLIAM CAMPBELL.

Dr. Sorby, of Sheffield, was the first to make rock sections and to examine them under the microscope by transmitted light. From the examination of the microstructure of rocks he was naturally led to that of meteorites, and as a preparatory study he started with the investigation of artificial irons, in 1863. His first paper on the subject was "On the Microscopical Photographs of Various Kinds of Iron and Steel," *British Association Report*, 1864, 2, p. 189, which was shortly followed by another "On the Microscopical Structure of Meteorites and Meteoric Iron," *Proc. Royal Society*, XIII., p. 333; and *British Association Report*, 1865, I., p. 139. For over twenty years this appears to have attracted no attention, but after the publication of his two excellent papers "On the Application of Very High Powers to the Study of the Microscopical Structure of Steel," and "On the Microscopical Structure of Iron and Steel" (*Journal Iron and Steel Inst.*, 1886, p. 140; 1887, I., p. 255), metallurgists began to see the possibilities of the use of the microscope in helping to unravel those problems in which chemical analysis had failed.

In 1878 Martens published a paper on the microscopical examination of iron,* which was followed after a long interval by one from Dolliak.† In America Bayles ‡ and Lynwood Garrison § had taken up the work, whilst in France Osmond and Werth's paper, "Structure Cellulaire de l'Acier Fondu," || appeared in 1885. In the same year Wedding read his paper on the properties of malleable iron deduced from its microscopic structure¶ before the British Iron and Steel Institute. From that date the new science has made great advancement, especially along the line of research in iron and steel. Alloys have been studied and their constitution and complete freezing-point curves explained. Rooseboom's presentation of the theory of solution and Gibbs's Phase Rule have been applied and are found to supplement and explain many of the structures met with under the microscope. This method of research is now being applied to almost all opaque inorganic bodies, both natural and artificial, and the results obtained are of such importance that a few notes on methods of procedure will not be out of place.

PART I.

As iron and steel are of the most importance and have received by far the greatest share of study, it is best to commence with them.

Preparation of Samples.

When we are dealing with a metal soft enough to be cut with a saw or turned down on a lathe, it is best to make a section about one half inch in diameter and one eighth inch or more thick. This can be very easily done by means of a hand- or mechanical hack-saw or when turning a testpiece down on the lathe.

When we are dealing with a hard, brittle substance, such as white cast iron, this is impossible, but we can always break off a fragment of about one half inch thick with a sledge hammer. The smoothest face of the chip is ground down on an emery wheel or grindstone until flat.

---

* *Zeits. des Ver Deuts. Eng.*, XXI., p. 11, 205, 481; XXIV., p. 397.

† "Beiträge zur Mikroskopie der Metalle," *Mittheil. über Gegenstände des Artillerie und Geniewesens*, 1883, 9, p. 467.

‡ *T. A. I. M. E.*, XI., p. 261.

§ *Ibid.*, XIV., p. 64.

|| *Comptes rendus de l'Acad. des Sciences*, Vol. C., p. 450.

¶ *Journal Iron and Steel Institute*, 1885, p. 87.

In cases where the cutting down a section to one eighth inch or more would produce a piece too small to handle, a block or base must be made. For sections of wires, Stead recommends a small piece of high carbon steel one fourth inch round by one tenth inch thick, drilled with a hole in the center just large enough for the wire to fit. The wire can be soldered at the back to the steel, but in doing so the face of the wire must be kept cool. The whole is then ground and polished in the usual way. In making sections of thin plates, Stead uses a piece of steel about one half inch square and one fourth inch deep. This is cut with a hack-saw about two thirds of the way through and the thin plate is inserted. The steel is then squeezed and the specimen held tight.

Grinding and Polishing of Samples.

The main object is to obtain a perfectly flat surface with a good polish, as free from scratches as possible. In the process of grinding and polishing, the surface of the metal must not be strained or distorted or its nature changed, for this will cause a modification or change which will show up when we come to develop the structure.

The methods of procedure followed by the different workers, Sorby, Martens, Osmond, Stead, Arnold, etc., vary in details, but they all aim to produce as perfect a polish as possible. Every one engaged in microscopic research finds out little methods of his own which he finds superior to all others.

*Sorby's method** was as follows: Slices one tenth inch thick were cut by a circular saw and the thickness was further reduced by filing or grinding in order that the final specimen might be of convenient size and weight. It was then permanently fixed to a piece of glass by means of hard Canada balsam. The upper surface was next made as flat as possible by rubbing on emery paper supported on a plate of glass. The first emery was coarse, whilst the last was the smoothest paper used in preparing steel plates for engraving. In some cases it was found that it was not possible to polish directly after using the first emery paper, because the surface had been greatly modified by the scratching. A Water-of-Ayr stone of very fine grain was used with water and the modified surface ground off until all traces of the scratches had been removed. The specimen was then polished on a wet cloth (with a

* *Journal Iron and Steel Institute*, 1887, I., p. 255.

wood back to keep it stretched smooth), first of all by means of the finest grained crocus and then by the use of the very best and finest washed rouge. A beautiful polish resulted, almost or altogether free from even microscopic scratches. When the constituents vary with each other very much in hardness they are worn down unequally and this shows up the difference in hardness between them. However, it is often necessary to have a perfectly level surface, with the hard parts flat and not rounded off at the edges. To accomplish this, Sorby polished dry, using rouge on a piece of parchment stretched on a sheet of plate-glass. He points out that some varieties of iron and steel then show their structure without further treatment, some of the constituents looking bright, colorless and metallic, whilst others appear dull and deeply colored.

The ordinary method of hand polishing is essentially the same as Sorby's. The chip of metal or specimen cut to size with a saw has one face smoothed as flat as possible on a file or grindstone. It is then rubbed on emery papers or cloths 1, 0 and 00, followed by French emery papers 0, 00, 000 and 0000 (Hubert). The latter papers are $13\frac{3}{8} \times 9''$ and can be cut up into three or four strips. It is best to mount the cloth or paper on flat hard boards $4 \times 14''$ or $4 \times 10''$, depending upon whether the paper has been cut into three strips longitudinally ($3 \times 13\frac{3}{8}''$) or four crosswise $3\frac{3}{8} \times 9''$). Starting with the coarsest paper, No. 1 commercial, the specimen is rubbed back and forth in one direction until all the file-marks or scratches due to the grindstone have completely disappeared. It is then rubbed on paper No. 0 commercial, but the direction is changed so that the new scratches are at 90° to those made by the last paper. The rubbing is continued until all the scratches from No. 1 have been obliterated, when the specimen is taken to the next paper No. 00, the direction again changed so that the new scratches are at 90° to those of paper No. 0 as before. This is continued through the four French emery papers, and the specimen is ready for the final polishing. It is always best to rub a new set of papers with a piece of hardened steel so that any coarse grains may be rubbed off. It is also advisable to wipe the specimen (and fingers) in passing from one paper to another, especially in the case of the last four papers, where the slightest grit leaves its mark on the specimen. Although difficult at first, one soon gets used to keeping the papers clean. The final polish is given on a piece of fine broadcloth (ribless) stretched taut on a

hardwood block and well moistened with water and well-washed rouge. Many people prefer to use blocks with diamontine powder or tripoli or both, between the last emery paper and the final rouge polish, but in most cases these are not necessary.

In all cases the rouge, tripoli or diamontine must be carefully washed free from coarse particles and grits. For very fine work it is often necessary in the preparation of polishing powders (and also of emery-powders) to classify them in sizes. This can be done by a method similar to that used by Schloesing for the analysis of kaolins.* The formation of lumps of coarse and fine particles in the process of levigation is due to the presence of carbonate of lime in tap-water. Schloesing therefore uses a preliminary treatment. He washes the powders to be classified with water containing about 0.1 per cent. nitric acid. This dissolves the carbonate of lime, etc., derived either from the water or from the powder treated. After the mixture has settled the clear water is run off and replaced by distilled water. After stirring well and once more settling this is repeated until all the acid has been removed. To help the suspension of the finest particles a little ammonia is now added. A syphon is introduced, with a hook at the end to prevent the portions which have settled from being stirred up again. The liquid is drawn off at the following intervals: Fifteen minutes, leaving all the coarse grains unsuitable for polishing; one hour, leaving a powder fit to start polishing; four hours, when a powder for polishing hard metals, such as iron, is obtained, twenty-four hours and eight days, when the finest polishing powders are obtained. The addition of a little acetic acid precipitates the last deposit in a few hours. The powders are best mixed with soap in the form of a paste.

Le Chatelier considers the best powders to use are the following: Alumina derived from the calculation of ammoniacal alum, commercial flour-emery, oxide of chromium derived from the combustion of ammonium bichromate, oxide of iron from the calcination of iron oxalate in air.

Mechanical Polishing Machines greatly reduce the labor in obtaining the required surface. An excellent machine has been designed by Stead and is shown in Fig. 1. It consists of a horizontal revolving wheel, which can be driven by hand or motor. There are several conical blocks with rings for securing in position the emery

* Le Chatelier, *Metallographist*, 1901.

papers, etc., and these are simply dropped into the recessed wheel and are carried round by friction. There is a shield around the polishing-wheel to catch any fluid thrown off during work. Above is a copper can for holding water, etc., fitted with a tap which allows the water or solution to drop on the center of the polishing blocks. Stead's method * of polishing a piece of steel containing .40 per cent. carbon is as follows:

The bar of steel is placed in a vise and one end is filed flat with a smooth file. A section one eighth inch thick is cut off by means of a mechanical hack-saw. A block carrying a No. 0 French emery paper is placed on the machine and the specimen pressed on the paper in one position until all the file marks have been obliterated and the scratches of the emery run all in one direction. The specimen is now turned through 90° and the process continued with less pressure until the scratches are again all in one direction. The process is continued with the second and third blocks carrying Nos. 00 and 000 French emery paper. The next block is covered with smooth black cloth. About one grain of diamontine powder is rubbed in and water allowed to drop onto the block. The specimen is pressed onto the block and made to traverse across it in order to obtain an even polish. When all the fine emery scratches have disappeared the specimen is ready for ordinary work, but for photography a finer polish is required. This is obtained on a block covered with chamois leather and fine gold rouge. The rouge is well rubbed in and the wheel is started. The coarser particles of rouge are got rid of by pressing the flat edge of a thin strip of steel on the surface of the block. The specimen is polished until the surface appears to have slightly lost its brilliancy, when it is ready for etching.

For finer structures the dry rouge block is replaced by one covered with parchment or by fine kid leather. The surface is first soaked in water and the rouge rubbed in under a stream of water which removes all but the finest particles. The polishing on wet blocks takes much longer than on dry ones, but the resulting polish is much better.

Professor Martens has designed a machine which polishes many specimens at the same time. This is shown in Fig. 2 (also taken from Stead's paper), which explains itself. His grinding plates or blocks are made of glass, cast iron, copper and lead, whilst his

* "Practical Metallography," *Cleveland Inst. Engineers*, February 26, 1900.

polishing is done on glass or pitch and sometimes on soft beds (of India-rubber, leather or cloth). He carefully levigates all of his grinding and polishing powders before use.*

Professor Sauveur's machine† carries four discs revolving in a vertical plane and covered with suitable cloths. They are easily removed and torn cloths renewed. In this design the four polishing surfaces can be used simultaneously, whilst a pair of water-

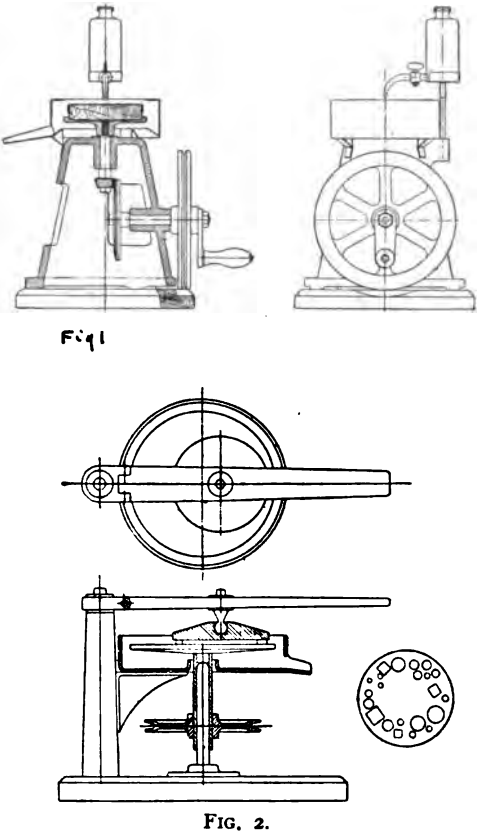


FIG. 2.

holders above are connected with tubes which direct a stream of water against the center of the discs. The outer disc is an emery wheel whilst on its back is the disc armed with fine emery powder. The second pair are usually covered with broadcloth and are

* "Method of Preparing Polished Surfaces of Iron and Steel for Microscopic Examination," J. E. Stead, *Journal Iron and Steel Institute*, 1894, I., 292.

† *Metallographist*, IV., 1901, p. 275.

rubbed with tripoli and rouge respectively. Sauveur claims that 15 samples or more can be polished in an hour if delivered to the operator after filing with a smooth file.

The method used in the Department of Metallurgy when several students are working together as shortly as follows. Specimen cut with hack-saw. One surface of section ground smooth on the grindstone. Made perfectly flat on emery-wheel of Sauveur machine. A disc, carrying No. 0 commercial emery paper, revolves on a horizontal spindle or axis. This is used after the emery-wheel in the ordinary way. The specimen is then rubbed by hand on boards carrying 00 commercial, 0, 00, 000, and 0000 French emery papers, after which it is polished on the rouge-wheel of the Sauveur machine, and is ready for the development of its structure. When a single operator is polishing several specimens much time can be saved by attaching all of the emery papers to circular discs which can be revolved on the horizontal spindle. Thus from the emery wheel we pass to the series of 6 discs carrying emery papers No. 0 and 00 commercial, and 0 to 0000 French. The polishing is usually finished on the last disc (rouge) of the Sauveur machine, but in many cases it is necessary to use the intermediate disc covered with tripoli powder in form of a paste with castile soap.

DEVELOPMENT OF STRUCTURE. — Having obtained a more or less perfectly polished surface it is necessary to develop the structure and in this we have the choice of several methods. Of these, etching is by far the most common, and usually the easiest to perform.

Iodine Etching. — Osmond and Le Chatelier use tincture of iodine for general work. A drop of the solution can be placed on the specimen and gently rubbed on with the finger to obtain uniform etching. Stead makes up the following solution: Iodine 1¼ gms. Potassium iodide 1¼ gms. in 1¼ c.c. of water and make up to 100 c.c. with alcohol; he also finds a second weaker solution, one fourth of above strength, very useful. One drop of solution per square centimeter of surface is put on the specimen and left there until the iodine color has disappeared. Wash with water, then alcohol and dry. If the etching is not sufficient the process can be repeated until satisfactory.

Nitric Acid Etching. — Sorby washed his specimens and etched them with very dilute nitric acid. He examined the specimen

under water and when he found that etching had gone far enough he washed the specimen in alkaline water and dried quickly. He usually wiped it with a soft handkerchief but in some cases found it necessary to rub the surface with very soft chamois leather to remove the film formed. Stead finds nitric acid less safe for steels than tincture of iodine, though in the absence of much phosphorus and arsenic it gives good results. He places the specimen in a dish containing 0.1 per cent. nitric acid (1.42 sp. gr.) in water and watches the process of etching through a strong lens. When etching is complete he washes well in running water, then in lime-water, again in water, then alcohol and dries. For rapidly developing structure Osmond recommends a 20 per cent. solution of acid (1.33 sp. gr.). Sauveur's method consists of immersing the specimen for a few seconds in nitric acid (1.42 sp. gr.) when the iron assumes a passive state. It is then placed under a stream of water which results in an evenly etched surface, quite free from the deposits of carbon common in etching with dilute acids, At the Mint, London, Roberts-Austen * used a very dilute solution (0.1%) of nitric acid in alcohol. After etching the specimen is immediately rinsed in alcohol and then rubbed with chamois leather dipped in benzene. The carburization and the heat-treatment of the steel determines the time necessary for etching; thirty seconds is sufficient for a very soft, low carbon steel whilst a quenched 0.8 per cent. carbon steel takes about two minutes.

For general work a 1 per cent. solution in alcohol gives very good results. The fluid is applied to the specimen by means of a glass rod with a soft rubber tip. The surface is rubbed until etching is deep enough, when the specimen is washed under the tap, rinsed in alcohol and dried in blast of air.

Other Reagents. — Le Chatelier † finds the following solution very superior. It consists of a ten per cent. solution of gaseous hydrochloric acid in absolute alcohol, with the addition of a quantity of anhydrous chloride of copper ($CuCl_2$) varying from 1 to 5 per cent. When dealing with hardened steel the smaller amount of copper chloride should be used. The quantity of solution necessary is about a drop or two to the square centimeter of surface and the etching is continued until a very light whitish-gray film appears. Wash in water, rinse in alcohol and dry quickly in current of dry air.

* "Sixth Report Alloys Research Committee," p. 17.

† *Journal Iron and Steel Institute*, 1902, I., p. 158.

Mr. Igevsky whilst working in Professor Le Chatelier's laboratory found that a solution of 5 per cent. of picric acid in alcohol gave the best results both for hardened and annealed steels, for unlike nitric acid, it does not color the ferrite (pure iron) in the least.

Of the other methods of developing structure two require special mention.

Osmond's "Polish Attack" is really a combination of polishing and etching. On leaving the rouge wheel the specimen is rubbed on a block covered with parchment, moistened with a solution of licorice root and calcium sulphate. By this method the various constituents of steel can be readily distinguished. Osmond and Cartaud * find that a dilute solution of ammonium nitrate (two parts by weight of the salt to 100 of water) answers the purpose better than the licorice and calcium sulphate, because the results are uniform and the solution keeps well. Osmond's beautiful photomicrographs are the best proof of the value of his "polish attack."

Heat-tinting has been used by Behrens and by Martens and consists of heating the specimen until its surface shows oxidation tints. It is the only method of distinguishing the phosphides from the carbides of iron. The surface of the specimen must be perfectly bright and clean. A small piece of sheet-iron is heated from below by a Bunsen burner. The specimen is placed in the center of the plate and heating is continued until the surface shows the requisite tint. The specimen can be quickly cooled in mercury, which checks further oxidation. Stead † has designed and used a simple electric heater, which can be fixed to the stage of the microscope, and the heat-tinting performed whilst the specimen is under examination. In his paper on Iron and Phosphorus,* Stead gives several valuable tables of heat tints and describes his own results.

MOUNTING. — When the top and bottom of the specimen are parallel it may be attached to the glass slide by Canada balsam. As a rule this is not the case. A very convenient mountant is plastic modelling wax. To obtain a perfectly level surface, the specimen is laid face downwards on a sheet of glass; a short brass cylinder is placed over it — the cylinder being turned down true

* *Metallographist*, III., 1900, pp. 1–3.

† *Journal Iron and Steel Institute*, 1900, II., p. 137.

and of such a height that the specimen does not project above it. Some wax is stuck on the glass slide, which is pressed down on the section until it rests on the brass ring. Instead of the brass ring, two equal piles of glass slides can be used, the specimen being laid between them.

As a temporary mount, Sauveur uses a small brass mount in which the specimen is held by an elastic band. This works well. When working with the microscope in a vertical position, Stead uses the following simple method: A short length of brass tube is cemented to a piece of glass. The tube is nearly filled with sand and placed on the stage. The specimen is placed face upwards on the sand and is pressed down by a glass slide until the latter rests on the brass tube.

For permanent mounting, a wax composed of resin, beeswax, red ochre and plaster of Paris answers very well. It remains plastic quite long enough to allow for levelling and then sets firm and hard.

To preserve the surface of the specimen, a cover-glass can be used with Canada balsam as for rock sections. This does not answer well for low-power work, because of reflected light from the surface of the glass. Stead covers the surfaces of his specimens with a solution of paraffin wax in benzole. For reëxamination the wax can be wiped off with a rag dipped in benzole. This has the disadvantage that the specimen must be cleaned each time before use. Le Chatelier recommends the use of "zapon," a solution of gun-cotton in amyl acetate. It forms a transparent film and the specimens can be examined even under the highest powers.

Microscope and Accessories.

Any good type of microscope can be used. It ought to have a firm solid stand to give rigidity, especially for high-power work. A revolving stage is an advantage, especially for examination with oblique illumination. A fine adjustment is necessary to get a sharp focus, whilst the stand should be such that the instrument can be used either in vertical or horizontal position.

As transmitted light cannot be used, the illumination must come from above. In using low-power objectives, the light is thrown onto the object by means of reflectors placed between the objective and the specimen. By means of the Sorby-Beck reflector (shown on the right in Fig. 3, fitted to a 1″ objective) we can ob-

tain oblique and vertical illumination. It consists of the parabolic reflector of Beck and a small mirror set at 45° to the horizontal, which can be turned out of use by means of the milled head. This is Sorby's mirror.

For oblique illumination, the Sorby mirror is thrown out of use. The horizontal rays of light strike the parabolic reflector, are thrown down onto the object at all angles but the vertical, and hence if the specimen be perfectly flat it will appear quite dark, for no light will be reflected into the objective. This is shown diagrammatically in Fig. 4. The oblique illumination shows up the structure of specimens polished in relief and surfaces broken up by

FIG. 3.

etching. In this way the pearly nature of eutectics is most beautifully shown.

For vertical illumination, the Sorby mirror is turned back into play and partly covers the objective. The horizontal rays of light (*L*, Fig. 5) strike the mirror set at 45° and are reflected vertically downwards onto the objective *O* and are again reflected vertically into the objective. Hence all flat parts of the specimen appear bright, whilst a broken-up structure has more or less shade. Where only vertical illumination is required a simple method has been devised by Stead. A thin brass tube, fitting over the end of the objective, is cut off at 45° to the vertical. Against this surface is fastened an ordinary thin cover-glass, which almost touches the end of the objective. Then, as before, horizontal rays of light

strike the cover-glass at 45°, are reflected vertically downwards onto the specimen and then upwards through the cover-glass into the objective.

For high powers the Beck illuminator can be used. This is shown in Fig. 3, on the left, attached to the objective and standing on its brass case. Like other illuminators for powers greater than two-third inch, it fits between the objective and the stem of the microscope. It is simply a short brass tube in which is fixed on a pivot a small reflector (a thin disc of glass) which can be set at any angle by the milled head. The light enters through the circular hole in the side. The glass disc is set at 45° with the vertical, the beam of light *L* (Fig. 6) enters through the circular hole in the side, strikes

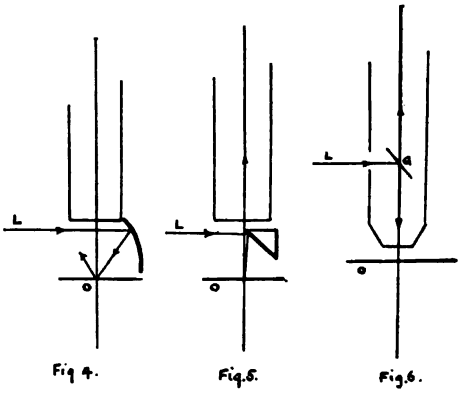


Fig 4. Fig.5. Fig.6.

the disc *G* at 45° is reflected vertically downwards through the objective onto the specimen *O*, and back again to the eye-piece. Thus we get vertical illumination. Instead of the Beck illuminator above the objective a right-angled prism, moving in a horizontal direction, can be used. Both Nachet and Zeiss make this form of illuminator, which gives very good results with one-fourth inch or one-eighth inch objectives. For the one-eighth inch or oil immersion the Beck seems to give the best results.

The multiple nose-piece which works so well with transmitted light becomes awkward when fitted with reflectors. For quick work, Zeiss' object glass slide changer is very convenient. It consists of a grooved slanting slide-holder fixed to the microscope tube and each objective is attached to a slide piece, which slips into position in the holder. Adjustment can be made by means of a small set screw.

A very useful microscope has been devised by Professor Le Chatelier.* It consists of a horizontal eye-piece tube, fitted to a firm tripod support, in the body of which is fixed a prism, so that the objective points upwards. Fig. 7 is a very diagrammatic sketch. The specimen to be examined, *O*, rests on a support which stands on a screw-collar whose fine adjustment gives sharp focussing. The face of the specimen points downwards to the objective *A*, and hence can be of any shape provided it has the one polished surface. The size of the specimen can also vary within wide limits. The illuminating beam of light *L*, passing through the tube of the microscope, strikes the illuminating prism *P*, is reflected through the objective *A* onto the specimen *O*, and

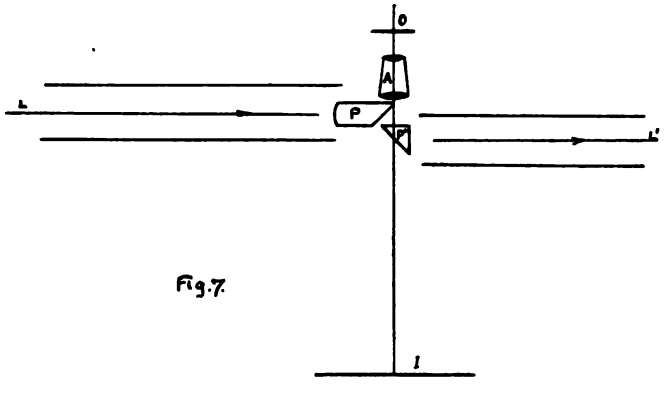


Fig. 7.

then passes back through *A* to the prism *P'* which totally reflects it along the eye-piece tube to the eye-piece at *L'*. The face of the illuminating prism *P* is really composed of two planes, one of them making an angle of 22.5° with the horizontal, the other a similar angle with the vertical, thus reflecting the horizontal beam of light *L* into the vertical. To photograph a specimen, a short camera is screwed onto the body of the microscope directly below the objective. For direct observation the reflecting prism *P'* covers the objective, but for photography the prism *P'* is drawn out of action, and the image is thrown onto the photographic plate I.

Illumination.

For all ordinary work an incandescent Welsbach gas burner gives good results. Acetylene gas jets have also been used. For

* *Revue Générale des Sciences*, January 30, 1897. *Metallographist*, IV., 1901, pp. 10–17.

high power work, especially with photography, an arc light gives the best illumination.* A "Brush" automatic light, working at an angle of 25° to the vertical, with the top carbon positive, using 10 amperes, has been found very satisfactory.* In any case, the rays of light are usually concentrated by means of a bull's-eye condenser placed between the source of light and the reflector. When using high-power objectives, especially oil-immersion, it is necessary to stop down the light by means of the diaphragms attached to the Beck and to the Nachet reflectors. When making a direct examination with an arc light for illumination the light must be cut down by placing a piece of tissue-paper, colored or ground glass between the bull's-eye condensor and the reflector, otherwise the eye will soon become seriously strained.

With the arc light, alum cells, etc., are used to absorb the heat rays, but at the Mint, London,* these are dispensed with. It was found that if a hole three-eighth inch in diameter be drilled in the brass tube of the Beck illuminator on the opposite side to that at which the light enters, very little heat is reflected through the objective. When the Nachet illuminator is used the light can be obtained from the filament of an incandescent electric lamp placed close to the slit. A 2 to 6 volts lamp gives the best results, for the filaments of higher voltage lamps are too thin to illuminate the whole field.

Photography.

In taking a photograph, the microscope takes the place of the camera lens. Any well-made camera will serve, provided the back is firm and rigid. Focussing on the ground-glass is done by means of a small lens. To obtain a sharper definition a piece of very thin glass is cemented onto the center of the ground-glass with Canada balsam. A still better method is to cement five cover-glasses to the ground-class, one in the center and one in each corner, thus making five transparent places where the focussing can be made accurately.

There are two methods of using the camera: In the horizontal position and in the vertical. In the first, the microscope is of course in the horizontal position and therefore the specimen must be firmly attached to the glass slide and fixed on the stage. For this method a mechanical stage is almost a necessity. The greater

* "Sixth Report to Alloys Research Committee," *Inst. Mech. Eng.*, London, 1904, p. 16.

the distance between the plate-holder and the microscope, the greater the magnification; the shorter the distance the sharper the image. So the length of bellows, etc., is a matter of personal preference. Roberts-Austen used a camera about six feet long, two thirds of which were collapsible bellows, the other third being a light tapering conical tube, so hinged that it could swing in a horizontal plane when it was desired to use the microscope for ordinary examination. For focussing, a thin rod ran parallel to the camera and was attached to the fine adjustment by means of

FIG. 8.

a thin cord and pulley. This method of course takes up considerable room.

When the microscope and camera are used in the vertical position much less room is needed, and a mechanical stage is not necessary. The length of camera is restricted however, and a very rigid camera stand is needed. Stead and others favor this method because of the simplicity with which the specimens can be examined. Most manufacturers of cameras make special cameras and stands which can be used in either position. The stand usually consists of two rigid bars attached to a cross-piece, which is hinged to a heavy metal base. The camera slides on the two parallel bars and can be clamped in any position. A wooden stand can be

made at a small cost and answers very well. Figs. 8 and 9 show a stand designed and made by Mr. E. J. Hall, which gave excellent results. It consists of a wooden base weighted with lead to give it rigidity. To it is hinged a wooden slide to which the camera can be clamped at any point. The camera shown is one of the ordinary long-focus type. Fig. 8 shows the microscope ready for use in the vertical position, with the camera swung out of the way, for observation. In Fig. 9 the camera and microscope are fixed ready to photograph in the horizontal position. Photographs can be taken with or without thc eye-piece. If the eye-piece is not used, care must be taken lest light be reflected from the sides of the microscope and fog the center of the plate. This can be avoided by a tube of black unglazed paper or black cloth.

FIG. 9.

Roberts-Austen* used a low power Zeiss projection eye-piece with Zeiss 35 mm. projection, the 24 mm., the 4 mm. with correcting collar, and the 2 mm. immersion objectives, which with the 6-foot camera gave magnifications of 50, 140, 850 and 1,600 diameters. Harbord, in his text-book on "Steel," shows a series of photo-micrographs at 150 and 1,500 diameters magnification, and these two powers give all that is necessary. For most work, however, it is seldom required to magnify above 1,000.

When the vertical method is used, or rather when the camera is movable, it is very convenient to have one arm of the support graduated. Then we can prepare a scale of magnification for each objective with the ground-glass at each particular position. The magnification can be found by using a micrometer on the stage

* Sixth Report Alloys Research Committee.

(and transmitted light) and measuring the image on the ground-glass in the ordinary way, but it must be remembered that the magnification varies with the distance between the eye-piece and the ground-glass — in other words the thickness of the specimen and mount must be taken into consideration.

The exposure necessary will vary with the brightness of the image and the light values. For ordinary plates, working with a Welsbach and 35 diameters magnification (1-inch objective, vertical illumination with Sorby-Beck reflector), the time varies from 20 seconds to one minute or more. A magnification of 120 diameters with the Beck illuminator, one to four or more minutes are required. With an arc light the time of exposure is greatly reduced. Harbord finds 15 to 20 seconds sufficient for 150 diameters magnification, and 1 to 1½ minutes for 1,500 diameters. However, correct exposure can only be learnt by experience. It will be found economical to use 3¼ x 4¼ inch plates, which can be easily fitted to the larger plate-holders by using adapters or "kits." The plates are developed in the ordinary way, but the developer should be one which will give a maximum amount of contrast especially when prints are wanted for reproduction.

As there is often some doubt as to what microscopic accessories are needed, the following list, given by Stead, may be useful: Three objectives (1-inch, ¼-inch and $\frac{1}{12}$-inch oil immersion); three eye-pieces (Nos. 1, 2 and 3), Sorby-Beck reflector for 1-inch objective; Beck's reflector (and Nachet's prism) for high powers; Bull's eye condenser; Zeiss object glass changers and a micrometer slide, 1 mm. divided into 1,000.

PART II.

When dealing with materials other than iron and steel, certain modifications have to be made in the method of treatment.

The *preparation of the metal* or alloy specimen needs some attention. If an examination has to be made upon the material as supplied, then a section of convenient size is cut as in the case of iron and steel. If too hard to cut, a chip is broken off. When we have to deal with a very brittle material, it is necessary to make a matrix or backing of some hard cement. If we have to prepare the alloy or metal by fusion, great care must be taken, because the final structure will in most cases depend upon the rate of cool-

ing, prevention of oxidation, thorough mixing when liquid, and the strains and stresses received when cold.

Rate of Cooling.—As a general rule, the slower the cooling, the fewer the points of initial crystallization, and the larger the structure, holds good for metals and alloys. In many cases, where we find metals and alloys rearranging themselves in the solid, this applies not only during solidification but also as the temperature of the solid falls to the normal. It is often advantageous to have a large structure, which can be examined under a low power objective, but it is often necessary to have very slow cooling, especially where we have a change or rearrangement in the solid state, in order that time may be allowed for the change or reaction to take place and a condition of equilibrium to be produced. There are many ways of obtaining very slow and uniform cooling. Where electricity can be obtained a resistance furnace can be used to advantage. Of the various designs, probably Howe's is the simplest.* It consists of two semi-cylinders of magnesia with a cover of the same material, and is heated by a spiral platinum wire fixed within the furnace. By placing the furnace in a jacket of lime, heat is retained and slow and uniform cooling insured. It is safely used up to 1100° C. Where gas-fired furnaces are used, automatic cut-offs can be set up. One of the best forms was designed by Heycock and Neville,† and is worked by a head of water increasing at a uniform rate. This head of water slowly shuts off the gas supply. Where the ordinary type of assay furnace is used, the alloy or metal may be melted in a smaller crucible set within a larger one with the interstices filled with charcoal. The furnace is filled up with ash and cinder, all draft shut down and doors closed and the whole allowed to cool slowly. In this way a very coarse structure can be produced.

To *prevent oxidation* a stream of coal-gas may be admitted to the crucible at the surface of the metal or alloy; but the simple way is to melt beneath a thick layer of hard granular charcoal. In making small buttons which melt at a low temperature where very slow cooling is not required, potassium cyanide is very convenient. Some of the salt is melted in a graphite crucible, the metal or metals are then added, and when melted the crucible is shaken round, withdrawn from the furnace and allowed to cool in the air.

* *T. A. I. M. E.*, 1901.

† *Trans. Chem. Soc. London*, 1898, No. 73, p. 714.

When the whole has cooled down, the crucible is placed under the tap, the cyanide is washed away and the button taken out. In the majority of cases stirring is not necessary, solution and diffusion soon producing a homogeneous liquid, but occasionally two metals form homogeneous liquid alloys only after much stirring or after casting and breaking up (or granulating) and remelting. However it is only experience can teach how to make alloys in the best way.

The button (or ingot, if we are studying the structure due to casting) can be cut with a hack-saw or if brittle, a fragment can be broken off as described above. A vertical section of the whole button must be obtained, for in many cases the structures of the top and bottom of the alloy differ, especially when the constituents differ in specific gravity. For example, in some of the alloys of tin and antimony, crystallization begins by the solidification of cubes of antimonide of tin (SbSn) which are much lighter than the mother-liquor and rise to the surface, forming a layer there. Again certain pairs of metals, as lead and zinc or lead and aluminium, do not alloy but form two distinct layers, the heavier at the bottom. Having obtained a section it can be ground and polished in the usual way, but when dealing with soft metals and alloys, the emery wheel as a rule tears the surface and often causes the outer layer to flow. When this is the case the surface is smoothed down on a file, using first a "second cut," then a "dead smooth." This can be done by holding the file in the left hand so that the tag rests on the bench and drawing the section downwards over the surface. In the case of lead, tin and other soft materials, the file must be kept perfectly clean or particles will cling to the file and tear the surface of the specimen, thus modifying the structure. The emery papers are used next and the last two, 000 and 0000 French, often give better results when used with oil. In some cases, even the emery paper causes a slight flow of metal, and then it is necessary to grind down on a flat, very fine-grained Turkey or Water-of-Ayr stone with water or oil, and to give the final polish with diamontine and oil, using the finger-tip. This is very slow and tedious but gives excellent results. If the specimen is decomposed by water, then oil must be substituted wherever water was used.

Development of Structure. — Where one or more of the constituents is colored, the structure can be seen after polishing. In most cases it is better, if not necessary, to develop the structure. This

can be done by polishing in relief, by etching and by heat-tinting. The latter cannot be used where a very fusible constituent is present, or where a slight reheating will modify the structure. Polishing in relief shows up the hard constituents and is very useful when studying bearing metals, etc. The etching material will vary with the specimen and it is only from experiment that the best material can be found. Dilute solutions must be tried first, and if they do not act, then stronger ones may be used. Le Chatelier* recommends the method of etching specimens "when subjected to the influence of an electric current in a solution which has no action upon the metal," as it is then possible to control the etching by regulating the intensity of the current. The main object is to etch so that some of the constituents are more or less attacked and colored, whilst others remain unaffected. For alloys rich in lead, acetic acid usually gives good results; for those rich in tin, very dilute nitric acid may be used; for aluminium rich alloys, caustic soda; brasses require stronger nitric acid, whilst the bronzes show up with nitric acid or hydrochloric acid solutions, but in the neighborhood of speculum metal ammonia may be used.

Surface Structure.—In the case of soft metals and alloys, it is always very difficult to obtain a good polished surface, for part of the metal spreads over the surface and hides the true structure. Much can be learnt from the surfaces of small cast ingots and sheets. If the metal is carefully skimmed during casting many beautiful structures will be seen when cold, or can be developed by careful etching. These structures are usually an indication of that of the interior, but may prove deceptive where transformations occur in the solid. Ewing and Rosenhain† have published some excellent photo-micrographs of surfaces obtained by casting on plates of glass or highly polished steel. As the glass is liable to crack, Hannover‡ substitutes mica. A circular hole is drilled in a piece of charcoal which is placed on a clean sheet of mica. The alloy is cast in this. If this does not give a good surface, the alloy is placed on a sheet of mica, is covered with potassium cyanide and heated to the melting point by a blow-pipe. Another sheet of mica previously heated, is then pressed down on the sur-

* *Metallographist*, Vol. IV., 1901, p. 7. See A. H. Sirks, *Koninkl. Akad. Wetensch. Amsterdam Versl.*, II., 1902; abstract in *Science Abstracts*, January 26, 1903, and *Metallographist*, VI., 264.

† *Phil. Trans. Royal Society London*, A, Vol. 193, 1900, pp. 353–377.

‡ *Bull. de la Soc. d'Encouragement*, Aug., 1900.

face of the alloy until the latter is solid. In this way a beautiful surface is obtained on top of the alloy.

Preliminary Examination.—In studying a series of binary alloys it is necessary to prepare a large number in order that no important points may be missed. It is often possible to make for preliminary examination the whole series in one alloy. This is done by melting the pure metals in separate crucibles, and very carefully pouring the lighter onto the surface of the heavier and allowing the whole to cool. They mix in the vicinity of their contact, diffusion takes place and when cold, a vertical section shows the whole series from one pure metal to the other. After examination horizontal sections are cut at required points and by analyzing the filings an approximate composition is obtained. The operation of making the alloy is never very easy and requires a good deal of care. In some instances, as in the case where a compound is formed heavier than the heavier metal, it is impossible to obtain correct results, but with the alloys of copper and tin, copper and aluminum, copper and antimony, etc., the method has worked very well. From these diffusion alloys, the main points of change can be determined and the necessary alloys made with this in view, thus reducing the total to a minimum. In a similar way the structure of the carbon iron series can be shown in one specimen. A piece of high carbon steel or of washed metal is heated in an oxidizing atmosphere and the outside is decarbonized. An oblique section of the surface is then made and on etching we see the whole series from the outside layer of oxide, through pure iron, low carbon steel, medium and high carbon to that part of the original which has remained unaffected and has suffered no decarburization. The reverse effect is obtained by cementing a low carbon alloy.

In the above notes, details have as far as possible been omitted, but the references given will furnish any further information necessary on special points. In the *Metallographist*, Vol. I. to VI., will be found many of the best original papers on the subject, whilst "Mineral Industry" reviews its progress each year. Since the above was written Osmond's work on the "Microscopic Analysis of Metals," edited by Stead,* has appeared and can be recommended especially to those interested in iron and steel.

* Lippincott Co.

ABSTRACTS.

NOTES ON RECENT MINERALOGICAL LITERATURE.

By ALFRED J. MOSES AND LEA McI. LUQUER.

I. CRYSTALLOGRAPHY AND GENERAL MINERALOGY.

Note on a connection between the molecular volume and chemical composition of some crystallographically similar minerals.

Prior, C. T.—*Min. Mag.*, XIII., p. 217, 1903. The author concludes that the crystallographically similar minerals have *groups* of elements crystallographically equivalent, such as:

CaC	is equivalent to		NaN
NaSi	"	"	CaAl
CeP	"	"	PbCr
YNb	"	"	CaW
Al_2Si	"	"	Cu_2As
$BeAl_2$	"	"	$SiMg_2$, etc.

In cases where the chemical molecule is very complex, the equivalence of certain groups may be only approximate, and that the replacement which may be effected without changing the crystalline form may depend on the "mass effect" of the other constituents of the molecule (suggested by Penfield).—L. McI. L.

Tschermak, G. — Eine Beziehung zwischen chemischer Zusammensetzung und Krystallform. *Min. Mitt.*, 22, 393.

There exists a necessity for a space relation between the structure of chemical compounds and their crystal form, and the repetition of equivalent directions in the crystal must correspond to a repetition of chemical units or groups. Such considerations can be made independently of any molecular hypotheses and rest purely on the facts. Consider merely as to crystallization the kind of symmetry and the number of equivalent directions and in composition merely the simplest formula. Single atoms or groups will be found conforming in number to the equivalent directions. For instance the dimorphism of calcium carbonate might be explained in this way: the rhombohedral crystals require three double directions in each molecule but as $OC\overset{O}{\underset{O}{}}Ca$ has only one principal direction calcite may be considered composed of crystal molecules each six chemical molecules. But for aragonite the necessary three directions perpendicular to each other are all indicated if two chemical molecules are united

$$Ca\overset{O}{\underset{O}{}}OC.OC\overset{O}{\underset{O}{}}Ca.$$

In molysite, Fe_2Cl_6, which is rhombohedral, the idea is grasped without

considering a molecular net. If we write $Cl_8Fe.FeCl_8$ this alone suggests the six chlorine atoms in three double directions.

It appears that the disposition to a definite kind of symmetry is often indicated in the chemical formula.

In the rhombohedral system the threefold arrangement is characteristic. In minerals of this system we have examples corresponding to a three-rayed type A_8B, A corresponding to sometimes one member as O, Cl, H_2O, at other times to a pair of these as Cl_2, $2H_2O$.

Alunite, $3Al(OH)_2KS_2O_8$.

Pyrargyrite, $3AgS.Sb$.

Proustite, $3AgS.As$.

Hematite, Fe_2O_8.

Corundum, Al_2O_8.

In the tetragonal the fourfold arrangement predominates such as A_4B.

Zircon, O_4Zr_2.

Rutile, O_4Ti_2.

Cassiterite, O_4Sn_2.

Zeunerite, $8H_2O$, As_2O_8, $(UO_2)_2$.

In the hexagonal a sixfold type, A_6B, can be assumed.

Sodium vanadate, $12H_2O$, VO_4Na_3.

Magnesium platinchloride, $12H_2O$, $PtCl_6Mg$.

In the isometric there is a grouping both on a threefold and a fourfold arrangement. Sometimes both are indicated as in Eulytite, $3SiO_4.Bi_4$. Oftener only one, especially the threefold, as in

Helvite, $3SiO_4$, BeMn.MnS.

Boracite, $3B_4O_8.Mg_2B_4O_6MgCl_2$.

Senarmontite, Sb_2O_8.

The fourfold is less common,

Tin iodide, $4I$, Sn.

The repetition of the known types of higher symmetry is always a fact of value for comparison and may be an aid in considering complicated compounds. If a complicated formula is found for a crystal of a high grade of symmetry of which the structure is not practical because of our inability to recognize the chemical constitution of the compound, the considerations of these types will often lead to a plausible structure. Furthermore, if there exist a choice between two complicated formulæ, if the crystal is of a high grade of symmetry, the use of these types may lead to the best choice.

For instance, Rose's old formula, $Sb_2S_7R_4$, for tetrahedrite is not valid because it rests on a supposition of isomorphism between univalent and bivalent elements. Later analysis lead to $Sb_4S_{13}Cu_{10}Zn_2$. An arrangement of this according to the type A_8B would be

$$3SbS_8Cu_8.SbS_4CuZn_2.$$

Scheerer's formula for nephelite, $Si_9O_{34}Al_8K_2Na_6$, and the later formula $Si_{11}O_{42}Al_{10}K_2Na_8$, arranged on the type A_6B, lead respectively to

$$6SiO_4.AlNaSi_3O_{10}Al_2K_2, \text{ and}$$

$$6SiO_4.AlNaSi_5O_{18}Al_4K_2Na_2.$$

A. J. M.

Gaubert, P.—Contribution à l'étude des faces cristallines. (Faces vicinales). *Bull. Soc. Minn.*, *27*, 6–58, 1904.

In a previous article (same journal *25*, 223–260) the author showed that crystals rapidly produced have simple forms which are independent of the surrounding medium and appear to be solely a direct result of cohesion.

When the crystallization is slower exterior influences intervene. The addition of a foreign substance often completely modifies the form though frequently the same faces persist with the corners and edges truncated and beveled, producing more or less developed faces. In this slower production cohesion and capillary action both are active.

The irregular figures and little pyramids often found in large numbers on faces can be attributed to concentration currents.

Hence a crystal shows three kinds of faces of growth : (1) Due to rapid crystallization (cohesion solely). (2) Due to slow crystallization (cohesion and capillary action). (3) Due to feeble concentration currents.

The solution faces may be simple but are usually complex.

The same crystal may show faces of growth of more than one kind and may even grow in one part while dissolving at another.

Vicinal Faces. — Often faces with simple indices are replaced wholly or in part by flattened pyramids, the faces of which do not obey the law of rational indices. The angles of these vary in different crystals and Scacchi called the phenomenon polyhedry. Websky gave the name vicinal faces to those crystal faces which have complicated indices near those of ordinary faces.

The author reviews the theories to explain vicinal faces and then elaborates his own theory as to their origin.

In lead nitrate, when concentration currents were visible, the crystals grew rapidly in simple forms but when these currents were too feeble to carry the layer from the starting point over all the face an irregular deposit resulted without any relation to the system of the crystal or its symmetry and apparently solely influenced by the direction of the concentration current.

More often however there is definite orientation of the newly deposited material in accordance with the symmetry of the crystal.

1. If the current is entirely lateral there is produced one or several faces making a slight angle with the crystal face. If currents come simultaneously on the entire contour there will be a central cross.

2. If the current is vertical there result one or several pyramids which may be quite irregular, striated and without plane faces.

The author in the discussion counts all relief figures not due to corrosion as vicinal pyramids and discusses:

(*a*) Irregular figures as exhibited on cassiterite, quartz, carborundum, barite, adularia. These are relief figures usually rounded and due to concentration currents.

(*b*) Regular figures. Reviews the figures on fluorite, galena, analcite, topazolite, spessartite, wulfenite, vesuvianite, cassiterite, octahedrite hematite, quartz, apatite, topaz, adularia, sphene, axinite.

The author reviews the observed relations between vicinal pyramids and optical anomalies. The frequent union of these is undeniable, but in certain cases the vicinal pyramids do not affect the optical characters and there appear to be therefore two classes of vicinal faces, one due to the fact that certain crystals, like the garnets, are formed of other crystals of lower symmetry than the whole, the other sort due to concentration currents.

Conclusions. — The vicinal faces are found in all crystalline systems. While they can occur on several forms, as in topaz, they often exist only on certain faces, as on the dodecahedron, in garnet. Usually the vicinal pyramids occur on faces with simple indices. That is, the simple faces which form when the crystallization is rapid, seem to become later when the carrying of material is very slow, more active centers of attraction than other faces, but as such vicinal faces are comparatively rare this paucity of material cannot be the sole cause for then they would always be present. They seem rather to result whenever there is a rapid deposition, but at the same time concentration currents which are too feeble to completely cover faces of a certain size. This would explain why little faces do not show the vicinal pyramids.

Many crystals show successive vicinal deposits of gradually diminishing extent, that is, are step-like, others are quite plane. In the latter case often striæ indicate that the difference is one of degree, the layers being infinitely thin.

The difference between the regular figures may lie in the capillary action which just as in ordinary crystallization may have no recognizable effect upon rapidly formed deposits which will then be irregular and dependent only on the concentration currents or if the layers are slowly deposited the effects of the capillary forces will be a regularity of some degree.

In all cases the vicinal pyramids have the symmetry of the substance.— A. J. M.

Goldschmidt, V. — Ueber Entwickelung der Krystallformen. *Zeit f. Kryst.*, *28*, 1–36 u, 414–451, 1897.

It is difficult to convey clearly in the space of an abstract the purpose and methods described in this highly interesting article, and the attempt here made is admittedly unsatisfactory.

A task of crystallography is to deduce mechanically the properties of the crystals from the properties of the particles. A natural order would be:

1. Find the mechanical laws chiefly by aid of crystal form;

2. Seek the relations between crystal form and properties of particles using and arranging records and projections of well-developed forms;

3. Bring these relations into formulæ susceptible of mechanical discussion;

4. Test by these formulæ whether definitions, hypotheses and formulæ thus far used can stand or must be modified.

In this way there should result the laws of form development and the possible forms in the order of their probability of occurrence, etc.

Certain preliminary hypotheses may be made.

"Every face is crystallonomically possible which is perpendicular to a direction of particle-attraction."

Every primary force goes from the center of gravity of the particle through the center of gravity of the molecules which form the particle. (Not proved. Will use it, and abandon if not satisfactory.)

Disturbing Influences. — Varying outer influences must be assumed, otherwise the same forms would always result. These influences we may assume to be relatively feeble in proportion to the primary force and may be called pulling down force. A comparison is a mote on one side of a fine balance which tips the entire balance.

As to the nature of these influences we only know that they are outer forces from which the crystal particle is independent. That they are weak is suggested by the fact that slight variations in composition of the mother liquor affect the resulting combinations. We may say: The pulling down force acts and furthers the differentiation of forms.

Conclusions Based on all Uninfluenced Forms of a Species.—Why draw conclusions from summation of all crystals of a kind rather than from individual combinations? We assume all calcite crystals as products of action of *equal* particle forces. It depends on outside considerations whether one or another face forms. The summation of all observed faces shows what the particle force, so far as our observation goes, is able to produce in faces.

Probability of Occurrence. — All observed forms are not possible *at the same time* nor equally probable.

The grade of probability rests on the frequency of observed occurrence.

The primary forms are most probable because they have the greatest forming force.

From these, others with lesser force are derived, hence with lesser probability of occurrence, and so on to a limit at which the forming force is so weak that feeble outer influences deviate the faces giving vicinal forms which are shut out from this discussion.

Certain preliminary definitions and statements are needed.

"Knoten" (Knots) Points in Zones. — At certain points, called "knots," the distribution of faces along a zone changes.

Free Zones. — If between two knots the distribution of points is not disturbed by any influence that portion of the zone is called a free zone.

Ranking of Knots, Primary, Derived and Equivalent Knots. — End knots of a highly developed zone fragment are considered as more important than those of a weakly developed fragment.

A knot, the center of several important rays, is more strong than one not such a center.

Also a distribution often permits conclusion that one of two end knots has a stronger influence than the other.

The starting point of a development we call a primary knot. Every face point can be a knot but its power in a mass decreases as it is further removed from those primary knots or points at which the development starts.

Knots showing equal action and surroundings are equivalent. Their distribution determines symmetry.

Höfe. — Around important knots the field is free of points, so markedly that by this they are easily found. Two causes possibly act together to produce this. Often this court is taken by vicinal faces, the origin of which is different from that of typical faces.

Zone Höfe. — Zones rich in faces often are point free on each side.

Gesammtbild, Formensystem. — The total picture is characterized by the distribution of knots and the series derived from them. The primary knots by position and intensity furnish for all crystals the Formsystem.

Since these (primary knots) cannot be derived they may be assumed as peculiar to the crystal-building particles, hence may be considered as primary forces acting as such outwards.

DISTRIBUTION OF POINTS IN ZONE, NUMBER LAW, FREE ZONES, ETC.

Number Law. — Distribution of points in a zone, after choice of unit, is expressed in rational number (pq). The law is clearest when any zone between knots is transposed to a zone with beginning and ending of enumeration in these knots. The knots determine a distribution and conversely the distribution finds the knots.

Simple Form of Number Series.—The numbers in a zone fragment are not directly comparable but become so when we make p or q of the end knots in every case o and ∞. This form of series we will call the *simple* number series. (It is indifferent whether p or q be used.)

Free Zones, Normal Series.—When the distribution of points is influenced only by the end knots, there results a free zone and a normal series. Such are rarely large. Usually series made abnormal at certain points by strengthening effect of an intersecting zone.

Normal series, reduced to the simplest form, *are alike in all systems.* The comparison of $p(h/l)$ or of $q(k/l)$ for the first five series may be written

$N_0 = 0, \infty$ $N_1 = 0, 1, \infty$ $N_2 = 0, \frac{1}{2}, 1, 2, \infty$ $N_3 = 0, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}, 1, \frac{3}{2}, 2, 3, \infty$ $N_4 = 0, \frac{1}{4}, \frac{1}{3}, \frac{2}{5}, \frac{1}{2}, \frac{3}{5}, \frac{2}{3}, \frac{3}{4}, 1, \frac{4}{3}, \frac{3}{2}, \frac{5}{3}, 2, \frac{5}{2}, 3, 4, \infty$.

Series 1 is far the most frequent. With increased complexity the frequency of occurrence of a series decreases and the disturbing influences increase and a perfect series N_4 is almost unknown.

Series are symmetrical in this way, that the right side of 1 contains the reciprocals of the left side.

In order to show that the probability of occurrence is as stated above some twenty-one zones of common species were considered arranging the occurring forms and finding 21 of o, ∞, 1; 20 of $\frac{1}{2}$, 2; 11 to 15 of $\frac{1}{3}$, 3, $\frac{2}{3}$, $\frac{3}{2}$; 6 to 8 of $\frac{1}{4}$, 4, $\frac{2}{5}$, $\frac{5}{2}$, $\frac{3}{5}$, $\frac{5}{3}$, 3 to 5 of $\frac{1}{5}$, 5, $\frac{4}{5}$, $\frac{5}{4}$; 1 to 2 of more complex.

$\frac{5}{3}$ and $\frac{4}{3}$ occurred only twice but in a more general average are as frequent as their reciprocals.

The Development of a Zone. — The basis is "every possible face is perpendicular to a force of particle attraction" or each face is produced and represented by a force in the direction of its normal.

M = center crystal. AB trace of zone plane on projection plane. MR and MP are the primary forces in direction and intensity, oblique and unequal. o and ∞ are the end knots of the zone.

If the primary forces act to build faces then there result o and ∞, *i. e.* the series $= N_0$.

If MP and MR act together they form the resultant MS and by it the face projected at 1. But 1 does not need for its building all of MP and MS but only equal proportions say $\frac{1}{2}$ or $\frac{1}{3}$ of each. The remainders can act together toward other sides or independently as face builders.

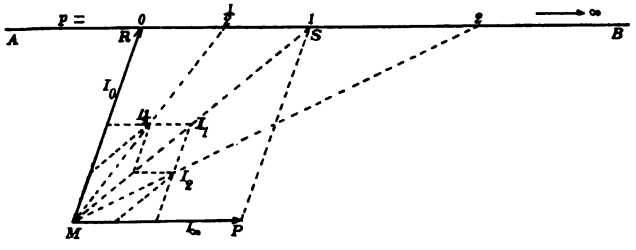
If now one portion of MP and MR is used in building of 1 and the rest for o and ∞ we get o, 1, ∞ the series N_1.

But the primary forces *MO* and *MR* may not only divide and unite with each other to form *MS* but portions of each may in turn unite with portions of the intermediate force *MS* and so on.

Let us *assume* the simplest case. The division always in two equal parts, the uniting always of one part from each side. This may be called normal complication.

Also *assume* every point can act with every neighboring point for complication, *i. e.*, every derived point can act in return individually as a knot.

The face projected at 1 would then be $i_1 = \frac{1}{2}i_0 + \frac{1}{2}i_\infty$. Now assume



point 1 to have become an independent knot feebler than the original 0 and ∞ in the ratio $i_1 : i_0$ or $i_1 : i_\infty$.

Now repeat the process of normal combination between the rest of l_0, *i. e.*, $\frac{1}{2}i_0$ and i_1. The halves of each give a resultant $i\frac{1}{2}$ and leave remainders $\frac{1}{4}i_0$ and $\frac{1}{2}i_1$. Point of projection is $\frac{1}{2}$. The same between i_1 and the residue of $i\infty$, the resultant of $\frac{1}{2}i_1$ and $\frac{1}{4}i\infty$ is i_2 with point of projection 2.

Hence from second normal combination we obtain 0, $\frac{1}{2}$, 1, 2, ∞ =. Normal series $2 = N_2$.

By a third combination between half of $i\frac{1}{2}$ and the half residue of i_0 results

$$\begin{aligned}
&\tfrac{1}{8}i_0 + \tfrac{1}{2}i_{\frac{1}{4}} = i_{\frac{1}{8}} \text{ projected at } \tfrac{1}{8},\\
\text{and between } i\tfrac{1}{2} \text{ and } i_1,\quad & i_{\frac{1}{4}} + \tfrac{1}{4}i_1 = i_{\frac{3}{8}} \text{ projected at } \tfrac{2}{8},\\
\text{“ } \quad \text{“ } \quad i_1 \text{ and } i_2,\quad & \tfrac{1}{4}i_1 + \tfrac{1}{2}i_2 = i_{\frac{3}{8}} \text{ “ } \quad \text{“ } \tfrac{3}{2},\\
\text{“ } \quad \text{“ } \quad i_2 \text{ and } i\infty,\quad & \tfrac{1}{8}i\infty + \tfrac{1}{2}i_2 = i_8 \text{ “ } \quad \text{“ } 3.
\end{aligned}$$

hence the third combination results in the numbers $\frac{1}{8}$, $\frac{2}{8}$, $\frac{3}{2}$, 3

0, $\frac{1}{8}$, $\frac{1}{2}$, $\frac{2}{8}$, 1, $\frac{3}{2}$, 2, 3, ∞ = Normal series $3 = N_8$.

A fourth combination gives in similar way

0, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{2}{8}$, $\frac{1}{2}$, $\frac{3}{8}$, $\frac{2}{8}$, $\frac{3}{4}$, 1, $\frac{4}{8}$, $\frac{3}{2}$, $\frac{5}{8}$, 2, $\frac{5}{2}$, 3, 4, ∞ .

= Normal series $4 = N_4$,

and so on to fifth, sixth, etc., combinations.

First Principle. — The probability and therewith the frequency of a number is the greater the nearer the number stands in development to the origin, i. e., the lower the order of the series in which it first occurs. Hence all in each of the following rows have equal rank:

In N_0, 0, ∞ ,
“ N_1, 1,
“ N_2, $\frac{1}{2}$, 2,
“ N_3, $\frac{2}{3}$, $\frac{3}{2}$, $\frac{1}{3}$, 3,
“ N_4, $\frac{3}{5}$, $\frac{5}{3}$, $\frac{2}{5}$, $\frac{5}{2}$, $\frac{3}{4}$, $\frac{4}{3}$, $\frac{1}{4}$, 4.

Second Principle. — For each derived number and the form belonging there is a certain intensity. The probability and frequency of a form is the greater the greater its intensity.

Goldschmidt shows that for equal primary forces acting perpendicularly to each other the rank by intensities is:

$$0\,\infty,\ 1,\ \tfrac{1}{2}\ 2,\ \tfrac{2}{3}\ \tfrac{3}{2},\ \tfrac{1}{3}\ 3,\ \tfrac{3}{5}\ \tfrac{5}{3},\ \tfrac{2}{5}\ \tfrac{5}{2},\ \tfrac{3}{4}\ \tfrac{4}{3},\ \tfrac{1}{4}\ 4,\ \text{etc.},$$

in which reciprocals are equivalent in intensity. This is however essentially the order brought out by the first principle. Observation checks this.

Hence the rank in a free zone fragment is essentially that determined by the grade of combination.

If the primary forces are unequal the calculation of intensities show numbers crowded more closely to the more intense knot and conversely in a free zone the points are crowded nearer the stronger knot.

Intensity and probability. — It may be assumed that a form is the more frequent the greater its intensity. Statistics are needed to show any exact relation.

Remodeling any series into the form $0 \ldots \infty$. Let p be the first member, p^2 the last, then each term of the $0 \ldots \infty$ series results from the corresponding number p of the given series by $(p - p_1)/(p_2 - p)$, for example in $1, \frac{4}{3}, \frac{3}{2}, \frac{5}{3}, 2$ the second term in the $0 \ldots \infty$ series is $(\frac{4}{3} - 1)/(2 - \frac{4}{3}) = \frac{1}{3}/\frac{2}{3} = \frac{1}{2}$ and the entire series is

$$0 \quad \tfrac{1}{2} \quad 1 \quad 2 \quad \infty.$$

A portion of a zone between two knots can thus be reduced to a $0 \ldots \infty$ series and it is then more easily decided whether it is distorted or normal. If when developed it is normal the reduced numbers will be in the normal order and there will be no strong points.*

If a zone is split between any two points, these reduced will give zones of lower order in each of which the abnormality is less marked. If finally by resplitting normal zones are reached the end numbers of the last zone fragments are the strong points or knots.

Four processes of remodeling are used:

1. Addition of a constant to each member of a series; this is equivalent to shifting the origin 0 to another place.

2. Multiplication by a constant. This is equivalent to altering the unit of force (or of zone line).

3. Inversion. Replacement of each by reciprocal. Reciprocal forms have the same significance.

4. Remodeling by $(p - p_1)/(p_2 - p)$ to $0 - \infty$ series as explained.

Example Topaz (the prism zone).

Form	a	f	ζ	N	M	O	m	λ	r	L	l	u
pq	$\infty 0$	6∞	4∞	2∞	∞	$\infty\frac{6}{5}$	$\infty\frac{3}{2}$	$\infty\frac{7}{4}$	$\infty\frac{13}{7}$	$\infty\frac{15}{8}$	$\infty 2$	$\infty\frac{11}{6}$
p	∞	6	4	2	1	$\frac{5}{6}$	$\frac{2}{3}$	$\frac{4}{7}$	$\frac{7}{13}$	$\frac{8}{15}$	$\frac{1}{2}$	$\frac{6}{11}$
Split	∞	5	3	1	$0\vert\infty$	5	2	$\frac{3}{5}$	$\frac{5}{8}$	$\frac{7}{9}$	1	$\frac{5}{6}$
Resplit					∞	4	1	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{7}$	$0\vert\infty$	5

*Points in vicinity of which there is a disturbance or irregularity.

Form	π	g	n	μ	b
pq	$\infty\frac{5}{2}$	$\infty 3$	$\infty 4$	$\infty 5$	0∞
p	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	$\frac{1}{5}$	0
Split	$\frac{2}{3}$	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{4}$	0
Resplit	2	1	$\frac{1}{2}$	$\frac{1}{3}$	0

The abnormal numbers appear to be 4, 5, $\frac{1}{6}$, $\frac{1}{7}$ and are therefore to be suspected and criticised. The faces corresponding have following criticisms.

f. The angles obtained do not lead to the symbol 6∞ (610).

O. Based on one unreliable measurement and another record of a single face.

r and *u*. Based on a short note without figure or description of face.

L. Figure and description suggest a vicinal face on $l\infty 2$ (210).

That is the faces indicated as abnormal are not well proved.

In a second portion the author considers especially the "formsystem" or totality of forms which space will not permit of here. — A. J. M.

Kolbeck, F. and Uhlich, P. — Untersuchung verschiedener Mineralien auf Radioactivität mittels des photographischen Verfahrens. *Cbl. Minn. Geol. Palae.*, 1904, 206.

In this preliminary paper the writers record the testing of some twenty-five substances with respect to their effect upon photographic plates. The Johanngeorgenstadt uraninite collected before 1793 was as active as that of recent date and more active than similar ore from Joachimsthal. All other Saxon uraninites except one from Doppiswalde were strongly active.

Among other uranium minerals tested the uranopilite and uranochalcite of Joachimsthal, the uranotil of Weisser Hirsch and carnotite exerted a strong influence and the uranocircite of Bergen and zeunerite of Weisser Hirsh a moderate influence. These were apparently free from uraninite.

Among the thoria minerals tested the thorite of Arendal and orangite of Brevig were strongly active, while the yttrotantalite of Ytterby, though often containing uranium, showed no influence on the plate. Other species optically active were uranogummite, autunite, torbernite, uranopilite, euxenite, polycrase and monazite.—A. J. M.

Bardet, M. G. — Essai de mesure de l'activité photographique de certains minéraux. *Bull. Soc. Franc. Minn.*, *27*, 63, 1904.

Endeavors to record the radioactivity, taking uraninite as 100, uses a diaphragm of copper pierced with a 1 cm. hole over which the mineral is placed, constant time of exposure, extra sensitive plates, constant time of development. Compares the depth of the image in a simple photometer —A. J. M.

Barker, Geo. F. — Radioactivity of Thorium Minerals. *Am. Jour. Sci.* IV., *16*, 161, 1903.

Author considers that the radioactivity of thorium is probably not a secondary or excited radioactivity due to associated uranium in these minerals.—L. McI. L.

Pisani, F. — Examen de plusiers minéreaux au point de vue de leur radioactivité. *Bull. Soc. Franc. Min.*, *27*, 58, 1904.

Pisani places a little disc of lead or other metal, pierced with a triangular hole, on a sensitive plate. The exposure is one to twenty-four hours. After development a feeble image is best seen by holding it at 43° to a sheet of white paper illuminated by a gas jet.

The results of over seventy tests are recorded. Of these 15 silicates, 12 tantalates or niobates, 13 arsenates or phosphates, 1 sulphate, 5 fluorites and uraninite gave definite images. Aside from the fluorites, most of the species contained uranium or thorium. Whether the minute amounts of these, however, explain the action or whether they also contain one of the two new radio-active substances is not certain. In the case of fluorites the colorless gave no result, the chlorophane only feeble after forty-eight hours, while the violet Cumberland gave a well-marked image after one hour.

Baskerville, C. — Action of Ultra-violet Light upon Rare Earth Oxides. *Am. Jour. Sci.*, IV., 16, 465, 1903.

Zirconium and thorium dioxides alone phosphoresced, the other oxides not responding. A number of minerals, containing different proportions of these two substances were tested, but none responded. — L. McI. L.

Brun, A. — Études sur le point de fusion des minéraux et sur les consequences pétrographiques et synthétiques qui en résultent. *Arch. des sc. phys. et nat.* Avril, 1902. Abstract in *Bull. Soc. Min.*, XXV., 370, 1902.

The fusion tests were made in an electric furnace, the instant of fusion being indicated by the crystalline fragment becoming spherical. The temperature was given by the fusible cones of M. Seger, indicating variations of 20° up to 1,850°. The results differ widely from those of Cusack and Doelter. Two tabulations are given: 1°. Those minerals whose fusion point coincides with that of the loss of structure. 2°. Those minerals whose fusion point does not coincide with that of the loss of structure. — L. McI. L.

INDIVIDUAL SPECIES.

Anthophyllite, see Fayalite.

Arsenic. — Native, from Montreal. Evans, N. N. *Am. Jour. Sci.*, IV., *15*, 93. 1903.

Found in the thicker portion of a vein, cutting the nepheline-syenite of Forsyth's quarry, near Montreal, associated with calcite and traces of realgar and pyrite. The material was very pure, in large masses (several pounds in weight), showing concentric layers of the "scherbenkobalt" variety. Probably formed by fumarole action. The third noted occurrence in Canada. — L. McI. L.

Warren, C. H. — *Am. Jour. Sci.*, *16*, 337, 1903.

Arsenic, found in considerably fissured, reniform masses, attached to the walls of a small pocket in dolomitic limestone at Washington Camp, Santa Cruz County, Ariz. Occurs in a faulted zone in the highly metamorphic limestone, and its origin is attributed to fumarole action. — L. McI. L.

Arsensulfurite. — Rinne, F. *Cent. f. Min.*, p. 499, 1902.

Name given to a mixture of sulphur and arsenic (Buchholtz, S, 70.75; as, 29.22) found in amorphous, brownish, thin crusts at the Papandajan volcano, near Garut, Java. Brittle, with a hardness of 2.5. — L. McI. L.

Artinite. — Ueber Artinit, ein Neues Mineral der Asbestgruben von Val Lanterna. *Cent. f. Min. Geol. u. Palaeon.*, 1903, No. 5.

Name given to a white hydrous magnesium carbonate, occurring in fibrous spherical aggregates, with formula $MgCO_3.Mg(OH)_2.3H_2O$. Named after Dr. Ettore Artini.

Astrolite. — R. Reinisch. Ueber Astrolith, ein neues Mineralien *Cbl. Min. Geol. Palæ.*, 1904, 108.

Greenish yellow little spheres of radiating fibers in the diabase of Neumark in Saxon Voigtland. The little spheres are found in three very different inclusions in the diabase siliceous shales, alum shales. and granular limestone, the material does not fill clefts like wavellite which it somewhat resembles but is completely imbedded, the spheres being usually 4–6 mm. in diameter always built of somewhat broad radial columns and without crystal form. Easily cleavable in one direction, the cleavage vitreous to pearly, translucent in splinters. Streak grayish white. H. 3.5, G. 2.78 melts B.B. quietly to a gray enamel, shows iron in beads, and is not noticeably soluble in HCl or H_2SO_4.

Under the microscope separates into little siskin green plates irregular in shape and not markedly pleochroic, and smaller approximately parallel plates with rectangular cross section markedly pleochroic. Concludes the former to be basal, the latter vertical sections of the same material which is apparently orthorhombic.

The analysis leads to a metasilicate formula

$$(Al_2Fe_2)Fe(NaK)_2(SiO_3)_5.H_2O.$$

The name Astrolith is in conformity with the name "Sternle" used by the quarrymen. — A. J. M.

Autunite and its products of dehydration (Meta-autunite). — Rinne, F. *Cent. f. Min.*, p. 679, 1901.

Autunite in thin sections, heated between 75°–85°, shows the development of a new structure by the production of doubly refracting bands, having the microcline appearance. To this second form the author has given the name meta-autunite. — L. McI. L.

Boothite. — *Univ. Calif. Bull. Geol.*, III., 191, 1903.

A new species, occurring in massive crystalline forms. Also fibrous and rarely in incomplete *monoclinic* crystals, related in form to melanterite and pisanite. Analyses yield formula $H_2O.CuSO_4\ 6H_2O$. Named after Prof. Edward Booth.

Bornite. — On the formula of. Harrington, B. J. *Am. Jour. Sci.*, IV., 16, 151, 1903.

Careful analyses of one Bristol, Conn., crystal and of massive specimens from five Canadian localities, all apparently pure material, yield results indicating formula Cu_5FeS_4. The old formula Cu_3FeS_3 was based on an analysis of Plattner in 1839 on Cornish crystals, which subsequent examination would indicate to be impure. — L. McI. L.

Botryogen. — Eakle, A. S. Note on the Identity of Palacheite and Botryogen. *Am. Jour. Sci.*, IV., 16, 379, 1903.

Recent investigations prove palacheite (described in *Bull. Dept. Geol., Univ. of Calif.*, III., 231, 1903), to be simply a pure and well crystallized

form of the rare sulphate botryogen. Cleve deduces the more correct formula for botryogen as $Mg(FeOH)(SO_4)_2 \cdot 7H_2O$ or $2MgOFe_2O_3 \cdot 4SO_3 + 15H_2O$, which was that given to palacheite. The crystallographic forms and constants for botyrogen should be taken from the recent description of palacheite (referred to above). Monoclinic; $a : b : c = 0.6554 : 1 : 0.3996$; $\beta = 117° 9'$; cleavage very perfect parallel to (010) distinct parallel to (110). — L. McI. L.

Carbides and Silicides. — Spencer, L. J. Crystalline forms of Carbides and Silicides of Iron and Manganese ("Ferro-manganese," etc.) *Min. Mag.*, *13*, 296, 1903.

Crystals divide themselves into two classes:

(*a*) rhombic prism-zone, with prism angle of about 67½°.

(*b*) pseudo hexagonal prism zone, with prism angles of 59°–61°.

1. The carbo-silicide of Mn and Fe crystals belong to the holohedral-orthorhombic class.

2. The "Spiegeleisen" crystals belong to either the orthorhombic or monoclinic systems, probably the former.

3. The silico-ferro-manganese crystals are probably holohedral-triclinic.

4. The "ferro-manganese" crystals are probably also triclinic and isomorphous with (3).

More measurements, however, are needed on better material for the whole group. —L. McI. L.

Cerussite and Phosgenite from the Terrible Mine, Custer Co., Colorado, Warren, C. H. *Am. Jour. Sci.*, 16, 337, 1903.

The cerussite is evidently an alteration product of the phosgenite and is interesting chiefly on account of the notable amount of $SrCO_3$ isomorphous with the $PbCO_3$ (SrO = 3.15).—L. McI. L.

Coloradoite. — *Geol. Sur. W. Australia Bull.*, No. 6, p. 27.

A new analysis of pure material shows Hg 50.40; Au trace; Ag 0.12; Te 49.48 = 100.00, yielding formula Hg_2Te_3 (the old formula being HgTe) G = 9.21 Occurs in large pure masses at Kalgoorlie.—L. McI. L.

Coolgardite, see Kalgoorlite.

Diamond. — Ludwig, A. Change of carbon into diamond. *Chemik. Zeit.*, XXV., 979, 1902.

Author shows that small crystals, having the luster, hardness, gravity, and index of refraction of diamond can be obtained by heating in the electric arc pulverized carbon on a spiral of iron wire, the heating taking place in hydrogen and under great pressure (3,100 atmosp.). The author is trying to develop this process commercially.—L. McI. L.

Hasslinger, R. v. — On the production of diamond by the fusion of silicates with graphite. *Monatsf. f. Chemie*, XXIII., 817, 1902.

Author uses a mixture corresponding to the composition of the diamond bearing breccia (Kimberlite) of the Cape, to which is added 300 grams of powdered graphite. Metallic Al and Mg are used in place of the oxides in order to obtain good fusion. The process is carried on in a crucible. After dissolving the fused mass, small, regular octahedra are obtained, which are undoubtedly diamonds, as proved by their hardness and combustion in oxygen.—L. McI. L.

Euxenite.—Lincio, G. Ueber das angebliche Vorkommen von Germanium in den M neralien Euxenite, Samarskite, etc. *Cbl. Min. Geol. Palae.*, 142, 1904.

The writer reviews the records and concludes that thus far germanium has only been found in minerals corresponding to sulphosalts, for instance franckeite 0.1 per cent. Ge., canfieldite 1.82 per cent. Ge., argyrodite 6.42 per cent. Ge. and an iron black mineral from Aullagos, Bolivia, with 4.99 per cent. Ge.

The author examines the euxenite and samarskite in which Ge. was reported and finds no traces.—A. J. M.

Fayalite *and Anthophyllite.* — Warren, C. H. *Am. Jour. Sci., 16,* 337, 1903.

A large pocket (250 pounds) of the rare mineral fayalite has been found in the pegmatite in the quarries at Rockport, Mass. Interesting chiefly due to the formation by mineralizing solutions of a reaction zone of a new fibrous amphibole, when in contact with the quartz of the pegmatite. Qualitatively this new anthophyllite is a pure iron silicate.

$$\underset{\text{Fayalite.}}{Fe_2SiO_4} + SiO_2 = \underset{\text{Anthophyllite.}}{Fe_2Si_2O_6}$$

Theories of origin are discussed.

Gold in meteorites. — Professor Liversidge at the September meeting of the Royal Society of N. S. Wales. Microscopic particles of a malleable, yellow metal, insoluble in nitric acid, having all the appearance of gold, obtained from certain Australian and European meteorites (siderolites), were exhibited by Professor Liversidge. A subsequent paper is promised.

Kalgoorlite. — Spencer, L. J. Mineralogical Notes on Western Australian Tellurides: the non-existence of "Kalgoorlite" and "Coolgardite" as mineral species. *Min. Mag.*, 13, 265, 1903.—Author suggests the probability that in these tellurides the gold and silver do not replace each other isomorphously, but are present in atomic proportions.

The great difficulties in obtaining pure massive material for analysis, and the frequent occurrence of mixed tellurides from these localities, have led the author to assume (after a critical discussion of former analyses) that *kalgoorlite* and *coolgardite* are mixtures of known tellurides and not new minerals.

$$\underset{\text{("Kalgoorlite.")}}{HgAu_2Ag_6Te_6} = \underset{\text{(Coloradoite.)}}{HgTe} + \underset{\text{(Petzite.)}}{2Ag_3AuTe_2} + Te.$$

$$\underset{\text{("Coolgardite.")}}{HgAg_{6.8}Au_{7.6}Te_{22.9}} = \underset{\text{(Coloradoite.)}}{HgTe} + \underset{\text{(Petzite.)}}{1.15Ag_3AuTe_2} = \underset{\text{(Calaverite.)}}{3.1AuTe_2} + \underset{\text{(Sylvanite.)}}{3.35AuAgTe_4}$$

—L. McI. L.

Kœnenite. — Rinne, F. *Cent. f. Min.*, No. 16, p. 493, 1902.

Color, red; may resemble carnallite, but differs in having fine cleavage; G. = 1.98; hexagonal rhombohedral. Composition: $Al_2O_3.3MgO.2MgCl + 8$ or $6\ H_2O$. Occurs at Volprichausen, Solling. Named after Dr. v. Koenen. — L. McI. L.

Krennerite. — Smith, G. F. H. Some new crystal forms in krennerite. *Min. Mag.*, *13*, 264, 1903.

By measurement with a three-circle goniometer, twenty-seven new forms were identified, which had escaped notice with the older methods of measurement. None of the peculiarities shown by calaverite (with the same chemical composition) were observed. The axial ratio was found to be: $a : b : c = 0.9369 : 1 : 0.5068$. — L. McI. L.

Molybdenite. — Moses, A. J. The Crystallization of Molybdenite. *Am. Jour. Sci.*

The only satisfactory measurements of molybdenite crystals hitherto made are those of Brown upon material from Frankford, Pa. The earlier measurements were discredited.

The following list sums up some recent measurements by Professor Moses.

Assuming the unit of Brown, viz., a pyramid *o* making an angle *co* with the cleavage equal 65° 35′ from which $c' = 1.908$ is calculated, the angles with the cleavage are as follows:

Basal pinacoid c (0001). Not observed except possibly on Enterprise crystal.

Prism m $(10\bar{1}0)$. Aldfield, Quebec, as part of striations; Warren, N. H., traces.

Pyramid p $(20\bar{2}1)$. Calculated angle 77° 13′.

Measured angles	Aldfield, Quebec	77° 18′
	Cape Breton	77 29
	Okanogan Co., Washington	76 59

Pyramid o $(10\bar{1}0)$. Unit angle, Frankford, Pa., 65° 35′.

Measured angles	Tilly Foster Mine	65° 29′
	Warren, N. H.	64 27

Pyramid t $(20\bar{2}3)$. Calculated angle 55° 45′.

The Warren, N. H., angles for this, 54° 43′, and unit are *relatively* close for these indices but low for the Brown unit.

Pyramid s $(20\bar{2}5)$. Calculated angle 41° 23′.

Measured angles	Enterprise, Ontario	41° 26′
	Okanogan Co., Washington	41 46

Pyramid u $(10\bar{1}4)$. Calculated angle 28° 51′.

On Okanogan, Co., Wash., the angle 29° 54′ was obtained, which was near these indices for $20\bar{2}5 = 41° 46'$.

Mohsite. — Colomba, L. Sur la mohsite de la Beaume. *Acc. d. scienze di Torino*, XXXVII., 11 mai, 1902.

Found in small crystals in albite veins. Occurring forms recorded, among them being the new scalenohedron $(5\bar{2}1)$. Considered by author to be an independent species (not ilmenite), approaching crystallographically senaite and eudyalite. — L. McI. L.

Mooraboolite. — Pritchard, G. B. *Victoria Naturalist*, *18*, 63, 1901.

Occurs as colorless, radiated aggregates in the cavities of a decomposed basalt, near Maude in the valley Moorabool, Victoria.

Crystals elongated orthorhombic prisms with flat pyramidal terminations; no cleavage; H. 6; G. 2.167–2.17. Analysis (E. O. Thiele):

SiO_2	Al_2O_3	CaO	Na_2O	K_2O	H_2O
48.024	28.684	0.42	11.239	3.031	9.8 = 101.68.

A zeolite close to mesotype. — L. McI. L.

Palacheite, see Botryogen.

Phosgenite, see Cerussite.

Proustite. — Lamplough, F. E. E. *Min. Mag.*, *13*, 294, 1903.

On some new forms prominently developed on crystals of Proustite. Specimens from South America showed the new forms $7\bar{3}\bar{3} = 10\ R$ and $9\bar{4}\bar{4} = 13\ R$. — L. McI. L.

Pyknochlorite. — Fromme, J. *Min. Mitt.*, 22, 69, 1903.

A new chlorite belonging to the clinochlore group, gray-green in color and massive or micro-crystalline. H. = 1–2, G. = 2.8314. Only partially decomposed in acids; yields a black slag before B. P. Analysis gives formula $10SiO_2$, $4R_2O_3$, $17RO$, $14H_2O$; R''' chiefly Al with little Fe, R'' chiefly Fe and Mg with little Ca and Mn. Occurs in gabbro on the Schmalenberg. — L. McI. L.

Rœsslerite. — Schulten, A. de. *Bull. Soc. Min.*, XXVI., 99, 1903.

Sur la rœsslérite et la wapplérite. Production simultanée de la rœsslérite et de la pharmacolite.

The author concludes that the crystals of wapplerite measured by Schrauf were rœsslérite of the formula $HMgAsO_4 + 7H_2O$; and that the wapplerite (analyzed by Frenzel) was a mixture of the arsenates of magnesium and calcium. — L. McI. L.

Sperrylite. — Nicol, W. and Goldschmidt, V. *Zeit. f. Kryst.*, *38*, 58, 1903.

The minute but brilliant crystals found at the Vermillion Mine, Algoma District Ontario, have been reëxamined and eleven new forms recognized as modifications on the dominant cube, and the previously recognized octahedron and dodecahedra 102 and 101. The work shows the possibilities in measurement with the instruments of to-day. The largest dimension on the largest face is given as 0.8 mm. and on others as low as 0.03 mm.

A discussion of the causes of deviation in the measurements of such minute faces brings out several interesting statements such as:

"The perfection of a face is a function of its absolute and relative size." Large faces are apt to be distorted because the layers beneath exert a varying influence during their development. The faces of smaller crystals are usually better formed, but below a certain size the faces are again poorer because

1. "The relatively small faces are derived by highly complicated causes." "They are movable like the leaves and twigs in the wind while the trunk is at rest."

2. With little faces the border is relatively large but it is at this border part, the edges and corners, that the particles are bounded on only one side by oriented fixed particles. The center of such a face is most nearly plane, the edges tend to rounding. Hence, if practically only rounded border occurs no sharp measurements are possible. — A. J. M.

Dickson, C. W. — Note on condition of platinum in the nickel-copper ores from Sudbury. *Am. Jour. Sci.*, IV., *15*, 137, 1903.

A careful investigation of the ore (almost pure chalcopyrite) from Victoria mine, twenty miles west of Sudbury, proves that the platinum is in

the form of sperrylite, and also confirms Walker's statement that the platinum is associated with the chalcopyrite in the nickel-copper ores. — L. McI. L.

Samarskite, see Euxenite.

Spodumene from San Diego County, California. — Schaller, W. T. *Bull. Geol. Univers. Calif.*, Vol. 3, p. 265, 1903.

A very complete chemical, crystallographic and physical description given. Average of several analyses shows chemical compour.ds to be:

SiO_2	Al_2O_3	Mn_2O_3	Li_2O	Na_2O	K_2O	Ign.
64.42	27.32	0.15	7.20	0 39	0.03	no loss = 99.51

The crystals are not twinned, as shown by the figures. — L. McI. L.

Kunz, G. F. — New Lilac-Colored Transparent Spodumene. *Am. Jour. Sci.*, IV., *16*, 264, 1903.

The crystals are of large size and great beauty, with color varying from deep rosy-lilac to almost colorless. Found in a coarse decomposed granite, near Pala, San Diego County, Calif., at which place remarkably large colored tourmalines are also found.

Crys'als similar in color, but much smaller, have been found at West San Bernardino, Meridan, Calif. Some could be cut for gems, but the surfaces are dull. Twinning about the *a* (100) face well shown. Prism angle (Penfield) = 93° 15′. — L. McI. L.

Baskerville, C. — Kunzite. *Science*, Vol. *18*, p. 303, 1903.

Name Kunzite given to the lilac-colored, gem-like spodumene, which shows a characteristic phosphorescence under the action of X- and Röntgen rays. — L. McI. L.

Vesuvianite. — Californite. Kunz, G. F. (communicated). *Am Jour. Sci.*, IV., 16, 397, 1903.

A new ornamental stone, occurring in a large outcrop on the South Fork of Indian Creek, twelve miles from Happy Camp, Siskiyou Co., Calif. Material is massive, hard, translucent, olive to grass-green, takes a fine polish and was at first taken for jade (nephrite) and is associated with serpentine. Analysis by F. W. Clarke proves it to be vesuvianite. Apparently the same mineral has been found in Burro valley, Fresno Co., and Selina, Tulare Co. (at this latter place very rich in color).—L. McI. L.

Wapplerite. — See Rœsslerite.

Zeophyllite. — Pelikan, A. *Sitz. d. Ak. d. Wiss. in Wien*, 111, 236, 1902. Abst. in *Bull. Soc. Min.*, 25, 260, 1902.

Found as vitreous, translucent and almost colorless masses of radiating crystals on basalt or mesotype. Rhombohedral terminations, but shown by etching figures to be in the trapezohedral class. Analysis (by Zdarek) yields formula $Si_8O_4Ca_4H_4F_2$. The mineral is somewhat close to apophyllite. — L. McI. L.

BOOK REVIEWS.

Quantitative Analysis for Mining Engineers. By Edmund H. Miller, Ph.D. New York, D. Van Nostrand Company, 1904. Pp. vii+137. Price, $1.50.

A modern text book of qualitative analysis, while intended primarily for mining engineers, the range of the book is sufficiently wide to serve the needs of the chemist in mill and smelter, as it covers all the operations ordinarily demanded in metallurgical laboratories.

The following chapter headings give a good idea of the scope of the work: Ionization, Mass Action, the Analysis of Magnesium Sulphate and the determination of alumina in alum, Coal Analysis, Ferric Ammonium Alum, Analysis of Iron Ore, Pig Iron and Steel Analysis, Determination of Manganese in Spiegel and in Manganese Ores, Determination of Zinc in Ores, Limestone Analysis, The Determination of Copper in Ores and Mattes, The Determination of Lead in Ores, The Determination of Antimony in Ores, The Determination of Arsenic in Ores, Slag Analysis Flue Gas Analysis and References to Additional Analyses.

The very explicit directions for the various analyses, accompanied as they are by explanations based on the modern theories of chemistry, cannot fail to aid greatly to a complete understanding of the underlying principles of the science as applied to analytical work, but must also be of great benefit in reaching the best results in the larger commercial methods which are based upon chemistry.

F. W. T.

Woodbridge School,

FORMERLY

School of Mines Preparatory School.

---

417 Madison Avenue,

Between 48th and 49th Streets, NEW YORK CITY

Twenty-second Year Begins October 1st, 1904.

THE school is well equipped with physical and chemical laboratories, in which the students are required to perform a complete set of experiments illustrative of their recitations in physics and general chemistry. A special laboratory is devoted to qualitative chemical analysis for advanced students.

Five hundred Students of Columbia School of Mines have been instructed in the Woodbridge School. Also a large number have been prepared for Massachusetts Institute of Technology, Stevens Institute, Sheffield Scientific School, Lawrence Scientific School, Troy Polytechnic Institute, Cornell University, and the Classical, Medical, and Law Departments of Harvard, Yale, Columbia and Princeton.

A summer school for students who have failed in June begins August 13th and coaches men for the Fall examinations. All classes are limited to five. College men are coached in Freshman and Sophomore Mathematics and Quantitative Analysis.

An advanced course for older students prepares them to enter the second year class. Last June one of our students received his degree in Electrical Engineering in three years.

SERIAL

The School of Mines Quarterly

vol. 25, 1903-04

DATE DUE | BORROWER'S NAME

IN U. S. A.